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Doctoral Thesis

**Epitaxial Growth,
Structural Characteristics,
and Electronic States
of Ytterbium Pnictides**

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The University of Osaka
Photophysics Laboratory

Yitong Chen

Abstract

Epitaxial Growth, Structural Characteristics, and Electronic States of Ytterbium Pnictides

イッテルビウムニクタイトのエピタキシャル成長、構造特性および電子状態

By Yitong Chen

Rare-earth pnictides (*REPNs*) are well known for their diverse magnetic and electronic properties originating from strongly localized $4f$ electrons [1,2]. In recent years, thin-film growth by molecular beam epitaxy (MBE) under ultra-high-vacuum conditions has emerged as a practical approach for fabricating high-quality single crystal samples of *REPNs*, particularly *RENs* [3-5] and *RESbs* [6,7]. However, the epitaxial growth of ytterbium-based pnictides remains challenging. Because Yb is unable to catalyze the dissociation of N_2 molecules, unlike many other rare-earth elements, an activated nitrogen source is required for the MBE growth of YbN [8]. As a result, epitaxial YbN thin films have not been reported to date. Meanwhile, Yb ions can adopt either divalent or trivalent states, giving rise to multiple Yb–Sb compounds with different stoichiometries [9]. So far, however, reports on Yb–Sb thin films have been limited to YbSb₂ [10], while thin films of other ratios between Yb and Sb remain unexplored.

In this study, we successfully fabricated high-quality single-crystalline YbN thin films for the first time using nitrogen-plasma-assisted MBE [11]. Photoelectron spectroscopy (PES) reveals that Yb ions are in a purely trivalent state and that YbN is semiconducting. Also, evidence of hybridization between the Yb $4f$ and N $2p$ states is found [12].

Meanwhile, a systematic growth study of Yb-Sb thin films was carried out, in which epitaxial growth of divalent compounds was achieved under both Yb-rich (Yb₁₁Sb₁₀) and Sb-rich (YbSb₂) conditions, while trivalent YbSb could not be synthesized. This could be attributed to the weaker electron affinity of Sb compared with lighter pnictogen elements and the comparatively low reactivity of the supplied Sb₄.

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Chapter 1

Introduction

The physical properties of the materials, such as electrical conductivity, magnetic orderings, optical transitions, etc., originate from the interplay among the crystal structure, chemical composition, and the fundamental degrees of freedom of electrons, i.e., charge, orbitals, and spins. Rare-earth pnictides are among the ideal systems for studying the relationship between the material's degrees of freedom and its physical properties: The combination of different *RE* and *Pn* elements, the composition with different *RE/Pn* ratios, and the fact that some of the *RE* elements can take more than one valence state, lead to a variety of crystal structures and electronic states in rare-earth pnictides, and thus give rise to diverse electronic, magnetic, and topological properties. Therefore, rare-earth pnictides have attracted sustained attention in solid-state physics research for more than half a century.

While powder samples or bulk crystals have been mainly used in studies on rare-earth pnictides in earlier studies, in recent years, the growth of thin-film samples by molecular beam epitaxy (MBE) method in an ultra-high vacuum system has been widely adopted as a solution for providing high-quality single-crystal samples of rare-earth pnictides, especially for those materials for which the growth of bulk single crystals is difficult.

In this study, our primary motivation is to investigate the structural and electronic properties of high-quality single-crystal thin-film samples fabricated by molecular beam epitaxy (MBE). We mainly focused on ytterbium mononitrides, for which the synthesis of single-crystal samples in both bulk and thin-film form was difficult, and on ytterbium antimonides, in which multiple compositions with different Yb/Sb ratios, Yb valence states, and unique properties occur, such as complicated band structure with Dirac nodal line in YbSb₂ and antiferroquadrupolar ordering in YbSb.

For YbN, by plasma-assisted MBE, high-quality YbN epitaxial thin-film samples have been successfully fabricated, and the completely trivalent state of Yb ions and semiconducting nature of YbN have been confirmed. The details will be discussed in Chapter 3.

For ytterbium antimonides, the MBE growth of YbSb was not successful, possibly due to the lower electronic affinity of Sb compared with lighter Pn elements, and the low reactivity of Sb_4 supplied from the Sb source. On the other hand, epitaxial growth of Yb-rich $Yb_{11}Sb_{10}$ was achieved in addition to the previously reported epitaxial growth of Sb-rich $YbSb_2$, and the band dispersion of $YbSb_2$ was observed by angle-resolved photoelectron spectroscopy (ARPES). The details will be discussed in Chapter 4.

In the present chapter, the general research background of ytterbium mononitride and ytterbium antimonides will be introduced.

1.1 background

1.1.1 Rare-earth compounds

Table 1.1: Electronic configuration of lanthanoids

Element	Atomic number	within $4d$	$4f$	$5s5p$	$5d$	$6s$
La	57	Xe core	0	Xe core	1	2
Ce	58	Xe core	1	Xe core	1	2
Pr	59	Xe core	3	Xe core	0	2
Nd	60	Xe core	4	Xe core	0	2
Pm	61	Xe core	5	Xe core	0	2
Sm	62	Xe core	6	Xe core	0	2
Eu	63	Xe core	7	Xe core	0	2
Gd	64	Xe core	7	Xe core	1	2
Tb	65	Xe core	9	Xe core	0	2
Dy	66	Xe core	10	Xe core	0	2
Ho	67	Xe core	11	Xe core	0	2
Er	68	Xe core	12	Xe core	0	2
Tm	69	Xe core	13	Xe core	0	2
Yb	70	Xe core	14	Xe core	0	2
Lu	71	Xe core	14	Xe core	1	2

In general, rare-earth elements refer to the elements in Group III of the periodic table,

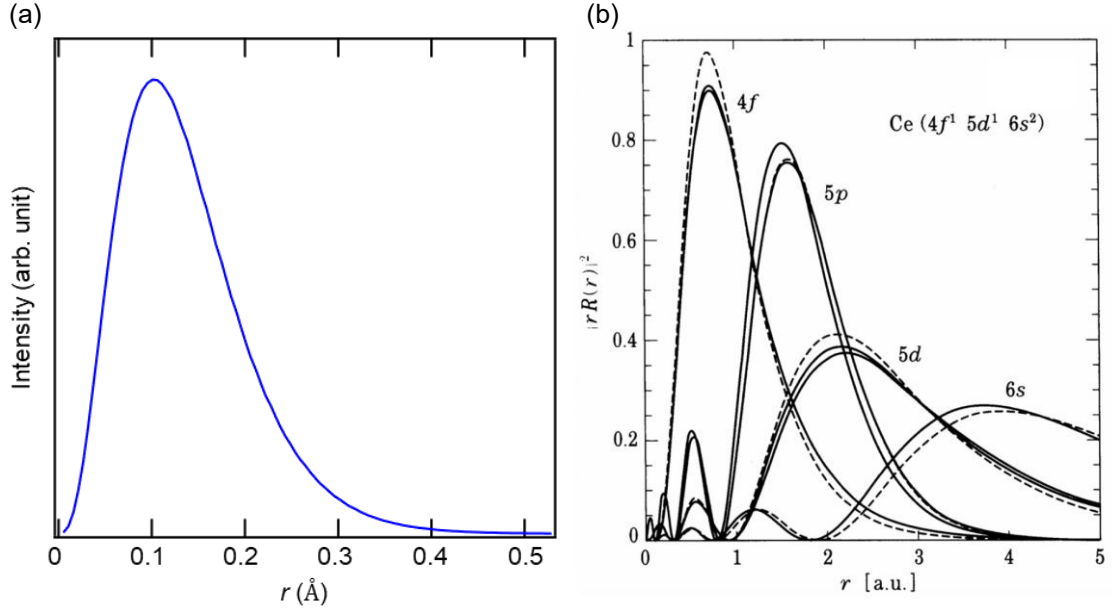


Figure 1.1: (a) The radial distribution function of Sm 4f electrons calculated using Bohr model. (b) Calculated radial distribution functions of Ce [1].

including scandium (Sc), yttrium (Y), and the lanthanoids beginning with lanthanum (La). In some texts, the definition of the rare-earth elements is more limited, suggesting only the lanthanoids with 4f electrons.

The properties of rare-earth compounds mainly originate from the interplay between localized 4f electrons and itinerant conduction electrons. The electronic configuration of the rare-earth elements (lanthanoids) is listed in Table 1.1. Although 4f orbitals have higher energy and 4f electrons act as valence electrons in rare-earth elements, they are located relatively close to the atomic nucleus, surrounded by the 5s, 5p, 6s, and 5d orbitals. Among them, the 5s and 5p orbitals remain fully occupied even when forming cations. Meanwhile, the radial extension of the 4f orbital is significantly smaller than the outer 5s, 5p, 6s, and 5d orbitals.

Assuming a hydrogen-like atom model (Bohr model), the electronic wavefunctions are expressed as

$$\psi_{n,l,m} = R_{n,l}(r)Y_l^m(\theta, \phi) \quad (1.1)$$

Here, n , l , and m denote the principal, azimuthal, and magnetic quantum numbers of the orbital, respectively. At the same time, $R_{n,l}(r)$ is the radial distribution function that

characterizes the probability amplitude of the wave function along the radial direction, and $Y_l^m(\theta, \phi)$ is the spherical harmonic function which determines the angular dependence of the wave function. For the case of a $4f$ electron, the radial distribution function is given by

$$R_{4,3}(r) = \frac{1}{768\sqrt{35}} Z^{9/2} \rho^3 \exp\left(-\frac{Z\rho}{4}\right) \quad (1.2)$$

where Z is the atomic number, $\rho = r/a_0$, and $a_0 = 5.292 \times 10^{-11}$ m is the Bohr radius. Figure 1.1 (a) exhibits the radial distribution function for samarium (Sm) derived from Equation 1.2 as an example. The full width at half maximum of the distribution function is approximately 0.14 Å, while the maximum is located at $r = 0.10$ Å. Figure 1.1 (b) shows the calculated radial distribution function for cerium (Ce) [1], where the Ce $4f$ orbitals evidently reside near the atomic core region, and with a smaller extension than the outer $5s$, $5p$, $6s$, and $5d$ orbitals. Since the $4f$ electrons are spatially located closer to the nucleus, they are strongly shielded by the fully occupied $5s$ and $5p$ shells. This shielding effect reduces the overlap between the $4f$ states with the orbitals that participate in chemical bonding. Therefore, the $4f$ electrons experience a strong effective attraction from the nucleus while hardly interacting with the surrounding crystal field.

The poor spatial overlap and strong screening effect lead to the highly localized character of the $4f$ electrons, which underlie the characteristic physical properties of rare-earth compounds, such as magnetic order and heavy-fermion behavior.

Since the $4f$ states are strongly localized, f electrons on neighboring ions do not significantly overlap with each other, and thus direct exchange interactions between the localized spins do not occur even in solids. However, an indirect interaction between localized f electrons mediated by conduction electrons, known as the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, is possible. The interaction between a conduction electron spin $\mathbf{s}$ and a localized f electron spin $\mathbf{S}$ is given by

$$\mathcal{H}_{cf} = -2J_{cf} \mathbf{s} \cdot \mathbf{S} \quad (1.3)$$

Since the interaction involves only the electron spin, the term $\mathbf{S}$ rather than $\mathbf{J}$ that expresses total angular momentum is used. Through this interaction, the exchange interaction between two f spin $\mathbf{S}_i$ and $\mathbf{S}_j$ is proportional to $-F(2k_F r) \mathbf{S}_i \mathbf{S}_j$. Here, $F(2k_F r)$ is the Friedel oscillation given by

$$F(2k_F r) \sim \frac{-2k_F r \cos(2k_F r) + \sin(2k_F r)}{(2k_F r)^4} \quad (1.4)$$

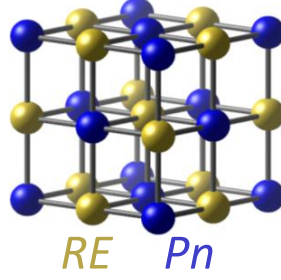


Figure 1.2: Crystal structure of $REPN$.

which decreases while oscillating with increasing distance r between $\mathbf{S}_i$ and $\mathbf{S}_j$. This exchange interaction (RKKY interaction) is thus effective over long distances. It can exhibit signs of both $+$ and $-$, leading to ferromagnetism or antiferromagnetism in rare-earth compounds. This leads to the application as permanent magnet material [2].

Meanwhile, there is another kind of interaction between the f electrons and the spin of the conduction electrons known as the Kondo effect, where the spin momentum of the $4f$ electrons is canceled (screened) by the spin of the conduction electrons. This antiferromagnetic interaction between the conduction electrons and the $4f$ electrons gives rise to heavy-fermion behavior, where the localized $4f$ electron and the conducting electron form an extremely heavy quasiparticle, whose effective mass could reach 1000 times that of the free conducting electrons, and participate in conduction [3].

1.1.2 Rare-earth pnictides

Rare-earth pnictides are compounds that consist of the rare-earth elements together with elements in group V (i.e., N, P, As, Sb, and Bi). When forming rare-earth pnictides, most RE elements are present only in the trivalent state. Meanwhile, europium (Eu), Samarium (Sm), Ytterbium (Yb), and Cerium (Ce) show different characteristics from the others: Eu, Yb, and Sm could act wholly or partly as divalent cations when forming pnictides, while Ce could be present in both trivalent and tetravalent states [4].

1.1.2.1 Rare-earth monopnictides

Within a variety of compositions of rare-earth pnictides, the 1:1 phase (rare-earth monopnictide: $REPN$) crystallized in the fcc rock salt structure (Fig. 1.2) is most common.

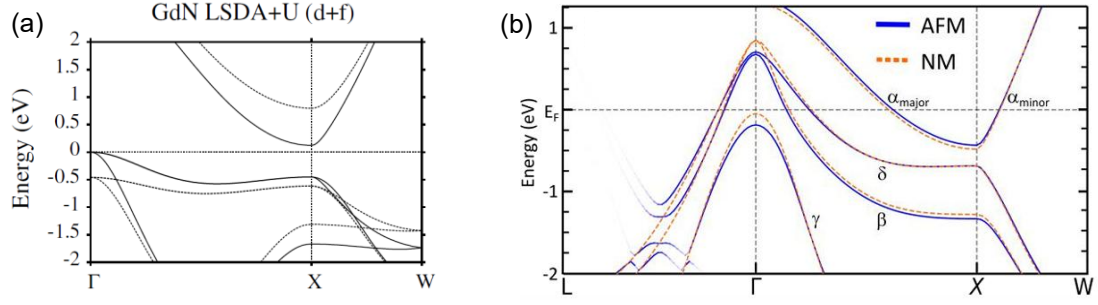


Figure 1.3: DFT calculated band structure of (a) GdN [5], and (b) GdSb in antiferromagnetic (AFM) and non-magnetic (NM) states [6].

Figure 1.3 shows the typical band structure of $RE Pn$. In general, the $Pn p$ band shows a maximum at the Γ point, while the $RE 5d$ band shows a minimum at the X point of the bulk Brillouin zone.

For $RENs$, as shown in Fig. 1.3 (a), the N $2p$ hole band is located below the Fermi energy, while the $RE 5d$ electron pocket is located above the Fermi energy, making them semiconductors with a band gap of about 1-2 eV. This was confirmed by both experimental and theoretical studies [5].

On the other hand, for $RE Pn$ with group V element except N, ($Pn = P, As, Sb, \text{ or } Bi$), both $RE 5d$ and $Pn p$ bands cross the Fermi energy, making them self-compensated semimetals. This complete electron-hole compensation further leads to the non-saturating extreme magnetoresistance (XMR) effect (Fig. 1.4) in $RE Pns$ [6–8], where the resistivity of $RE Pn$ can increase by more than 10000 times when a magnetic field is applied.

Table 1.2: Magnetic properties of rare-earth nitrides (RENs) extracted from Ref. [5].

Nitride	Pre 1994				1994–2013			
	Magnetic order	$T_C, T_N, \text{ or } T_h^P$ (K)	μ_{eff} (μ_B)		Magnetic order	$T_C, T_N, \text{ or } T_h^P$ (K)	μ_{eff} (μ_B)	
LaN	—	—	—		—	—	—	
CeN	No order	—	—		—	—	—	
PrN	VV PM	0–11	3.57–3.7		—	—	—	
NdN	FM	27.6–35	3.65–3.70		—	—	—	
SmN	AFM	< 2, 3, 18	—		FM	20–30	—	
EuN	VV PM	—	—		VV PM	—	—	
GdN	FM	62–72, 90	8.15–8.6		FM	25 (GdN/NbN), 58, 30–60, 61, 70	7.92, 7.0, 6.88, 6.8	
TbN	FM	34–42	9.3–10		FM / AFM	48, $T_N=31, 44$	8.5	
DyN	FM	17–26	10.5		FM	21, 25	—	
HoN	FM	13.3–18	10.8		FM	18	—	
ErN	FM	3.4–6	9.4		FM	7.5, 6.3	9.0	
TmN	PM	< 1.3	7.6		—	—	—	
YbN	AFM	0.73, < 2	4.44, 4.8		AFM	~ 0.5	—	
LuN	—	—	—		—	—	—	

Because of the strongly localized $RE 4f$ electrons, most $RE Pns$ show magnetic order at low temperature. As shown in Tables 1.2 and 1.3, while the REN family is dominated by

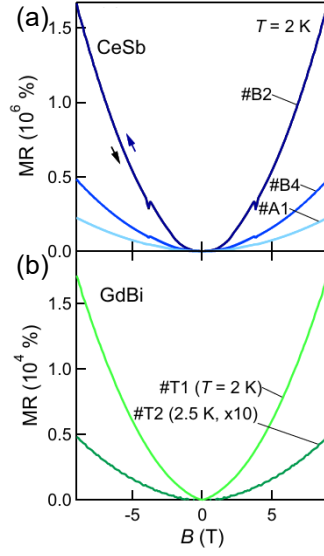


Figure 1.4: XMR in (a) CeSb, and (b) GdBi [7].

ferromagnets, the majority of other *REPNs* with heavier *Pn* elements are antiferromagnets.

The most famous phenomenon associated with magnetic order in *REPN* is the complex magnetic transition in CeSb, known as the "devil's staircase." CeSb shows an antiferromagnetic ground state at low temperatures. As shown in Fig. 1.5, as temperature goes up, CeSb undergoes a step-like transition through 6 different antiferro-paramagnetic states with different periods before finally transferring into a paramagnetic state. Similarly, when a magnetic field is applied, a stepwise transition through the antiferromagnetic states to the ferromagnetic state was also observed [10]. The origin of these anomalous magnetic transitions of CeSb was attributed to the mixing mechanism of the Ce $4f$ and Sb $5p$ states [11].

Also, the magnetic properties of *REPNs* lead to potential applications. For example, insulating GdN with ferromagnetic ordering at a comparatively high temperature of around 70 K is considered a promising material for use in electronic or spintronics devices, such as spin-filter Josephson junctions [13–18].

In addition to their electric and magnetic properties, theoretical [19, 20] and experimental [19] studies have suggested that *REPNs* may also host topologically nontrivial surface states. As shown in Fig. 1.6, when heavier *Pn* elements are involved, the increasing spin-orbital interaction makes a bigger splitting of *Pn p* bands at the X point of the Brillouin zone. This further leads to the reduction in the band gap at the X point. When the splitting is large

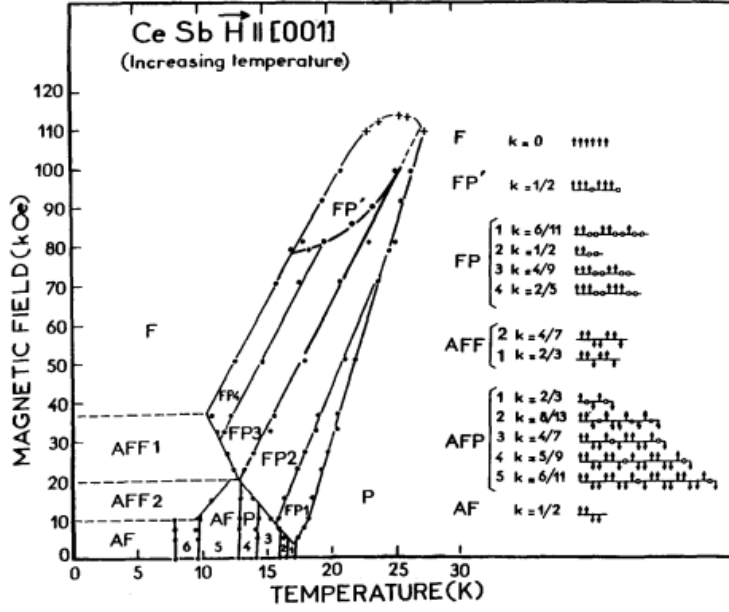


Figure 1.5: Magnetic phase of CeSb [12].

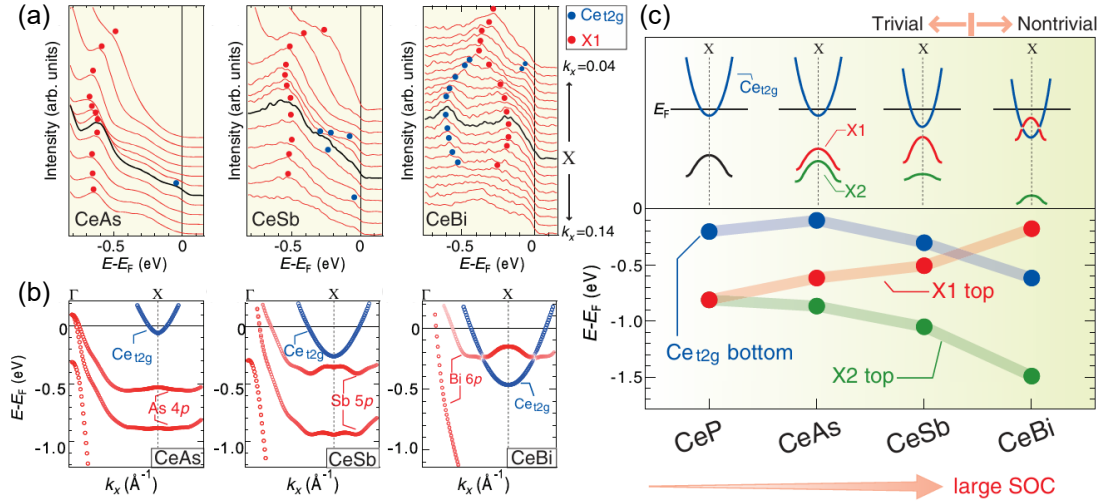


Figure 1.6: (a) Momentum distribution curves (MDCs) of ARPES on CePns near the X point. (b) Calculated band structure of CePns near the X point. (c) Schematic illustration of the topological phase diagram of CePns near the X point [19].

Table 1.3: Magnetic ordering and transition temperatures of rare-earth monopnictides extracted from Ref. [9].

Compound	N	P	As	Sb	Bi
La	No order	—	—	—	—
Ce	No order	AFM-I (8 K)	AFM-I (7 K)	AFM (6 K)	AFM (5 K)
Pr	—	—	—	—	—
Nd	FM (27–35 K)	AFM-I (19 K)	AFM-I (15 K)	AFM-I (11 K)	AFM-I (9 K)
Sm	AFM (< 3 K)	AFM (9 K)	AFM (8 K)	AFM (6 K)	AFM (5 K)
Eu	—	—	—	—	—
Gd	FM (58–70 K)	AFM-II (15 K)	AFM-II (18 K)	AFM-II (24 K)	AFM-II (25 K)
Tb	FM (34–42 K)	AFM-II (13 K)	AFM-II (12 K)	AFM-II (11 K)	AFM-II (10 K)
Dy	FM (17–26 K)	FM/AFM (9 K)	AFM-II (10 K)	AFM-II (9 K)	AFM-II (8 K)
Ho	FM (13–18 K)	FM/AFM (6 K)	AFM-II (7 K)	AFM-II (6 K)	AFM (5 K)
Er	FM (3–6 K)	AFM-II (5 K)	AFM-II (6 K)	AFM-II (5 K)	AFM (4 K)
Tm	No order (< 1 K)	—	—	—	—
Yb	AFM (0.5–2 K)	AFM (1 K)	AFM (1 K)	—	—
Lu	—	—	—	—	—

enough, the band inversion of the *RE* 5*d* band and the *Pn* *p* band finally occurs, suggesting the existence of topological surface states within the gap between the inverted bands. This non-trivial band topology was further confirmed by calculating the Z_2 index ν_0 [21] at the time reversal inversion momenta (TRIMs) [19].

Furthermore, a recent study suggested the possibility of realizing new quantum phases arising from the synergy between nontrivial band topology and magnetic order in *REPN*. As shown in Fig. 1.7, in NdBi and at low temperature, the massive and massless Dirac cones appear in domains with spins aligned out of plane and in plane, respectively [22]. This result indicated that the antiferromagnetic topological insulator state was achieved, opening a new venue for research on *REPNs*, to explore exotic quantum phenomena such as Majorana fermions [23].

Over the past two decades, compared to bulk samples, thin-film *REPN* samples fabricated in an ultrahigh vacuum environment, especially by molecular beam epitaxy (MBE), have attracted increasing attention. This is because MBE growth usually provides better cleanliness and better control of stoichiometry. Meanwhile, they are also more suitable for the fabrication of potential devices and allow the introduction of biaxial strain from the substrate.

So far, numerous studies on the MBE fabrication of *REN* [5], *REAs*, and *RESb* [24] thin-film samples have been reported, among which the growth of *REN* and *RESb* has attracted greater research interest in recent years.

For *REN*, many samples, particularly the early bulk samples, suffered from poor crys-

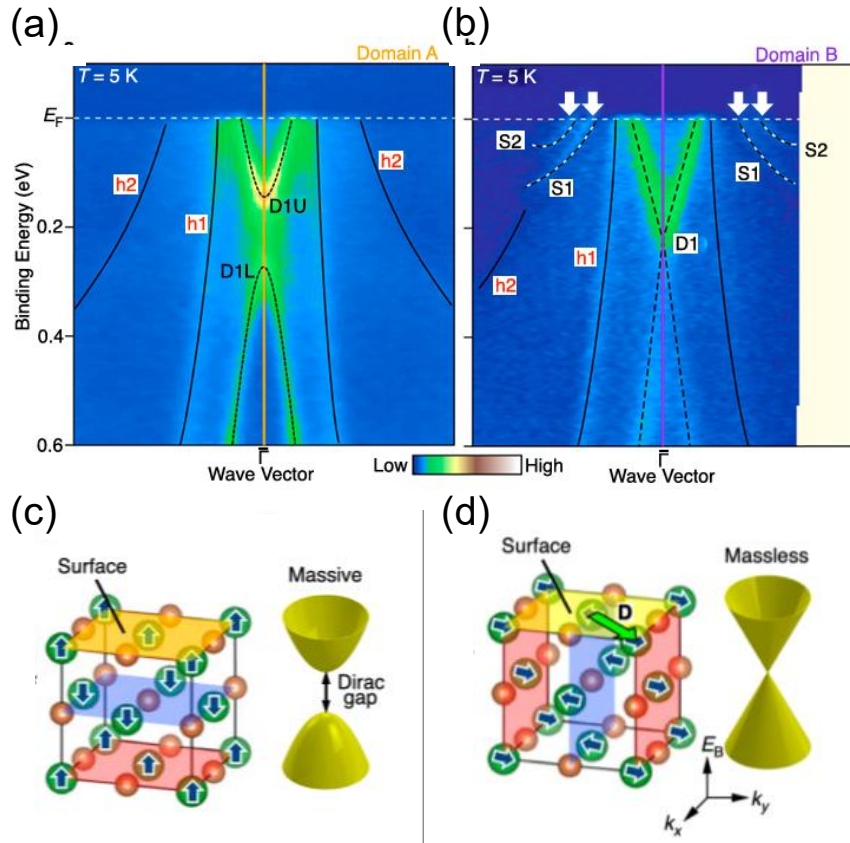


Figure 1.7: (a-b) ARPES intensity plot for domains A and B in NdBi. (c-d) Schematic illustrations of the antiferromagnetic order and the band dispersion of Dirac bands for domains A and B in NdBi [22].

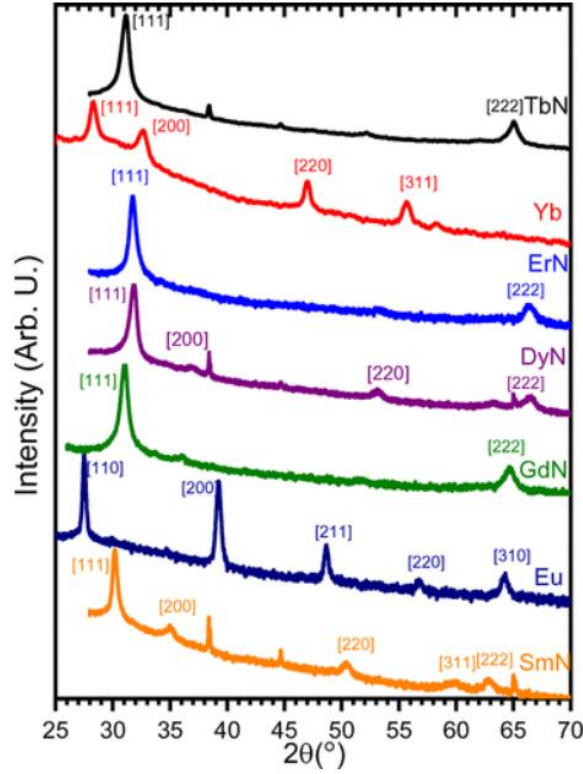


Figure 1.8: XRD ω - 2θ scans of thin films fabricated by depositing *RE* atoms at ambient temperature in a N_2 atmosphere [27].

tallinity, off-stoichiometry, or partial oxidation. Meanwhile, the theoretical predictions of the electronic structures and properties of *REN*s are also difficult, because of the necessity of treating the strongly correlated *RE* 4*f* states together with the widely extended N 2*p* and *RE* 5*d* states at the same time. These facts resulted in the debate over whether *REN*s exhibit semimetallic or semiconducting behavior [25, 26].

On the other hand, MBE growth of *REN* thin films is considered an easy yet effective approach to addressing this problem. Most *RE* atoms can catalyze the breakdown of molecular nitrogen even at room temperature, allowing *REN* layers to form on the substrates simply by depositing *RE* atoms in an N_2 atmosphere [27]. As shown in Fig. 1.8, "trivalent" *RE* atoms like Tb, Er, Dy, Gd, and Sm could directly react with nitrogen molecules to form a rock salt structured mononitride, while the "divalent" Yb and Eu cannot. By making use of this catalytic breakdown effect, research on *REN* is significantly accelerated. Up to now, in addition to polycrystalline GdN [14, 28–30], SmN, DyN, ErN, and LuN films [31, 32], epitaxial GdN [33–36], SmN [35–42], DyN [36], and HoN [43] films are also reported.

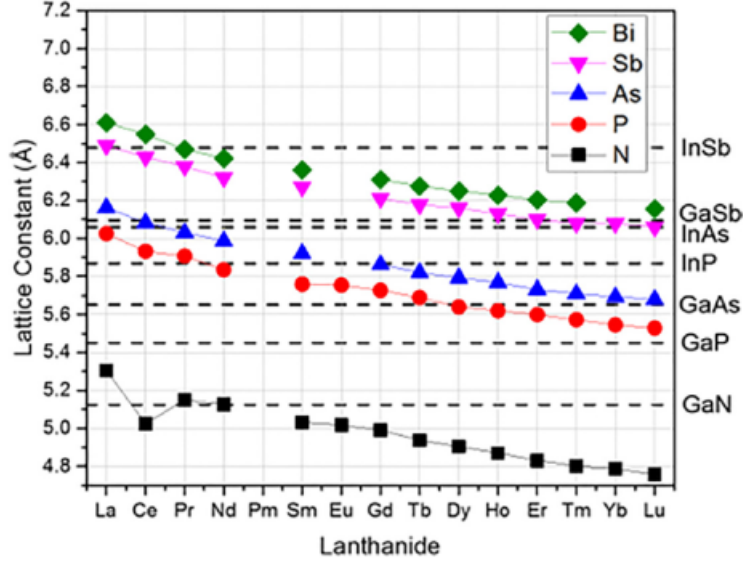


Figure 1.9: Lattice parameter of REP_n and common III-V semiconductor substrates [24].

However, the fabrication of samples perfect in both crystallinity and stoichiometry remains challenging because of the need for an ultra-clean environment, moderate growth rate, and carefully controlled growth parameters. Also, from these growth results, $\text{LaAlO}_3(100)$ and $\text{MgO}(100)$ substrates are confirmed to be suitable for the epitaxial growth of (100)-oriented REN thin films, despite the comparatively large lattice mismatch of about 10 % and the potential risk of oxidation due to the oxygen from the substrates at high substrate temperatures [40–43].

For the MBE growth of $RESb$ s, in addition to the earlier reported CeSb [44], and the embedded growth of ErSb on GaSb substrates [45], epitaxial growth of high-quality LuSb [46] and GdSb [6] epitaxial thin films are reported recently. This is facilitated by the good lattice matching between $RESb$ s and III-V compounds. As shown in Fig. 1.9, the lattice parameter of $RESb$ varies from approximately 6.5 Å to 6.1 Å when the atomic number of RE increases from La to Lu, making all $RESb$ s fit well in the lattice parameter to either GaSb or InSb substrates.

Furthermore, recent theoretical studies suggested that the possibility of controlling the band topology of $RESb$ by epitaxial strain [47, 48]. While $REAs$ and $REBi$ are trivial semimetal and nontrivial topological semimetal, respectively, $RESb$ is considered to be close to the boundary between the two states [19, 20, 49], whose band structure can possibly be tuned by applying small perturbations such as several percent of biaxial strain in an epitaxial

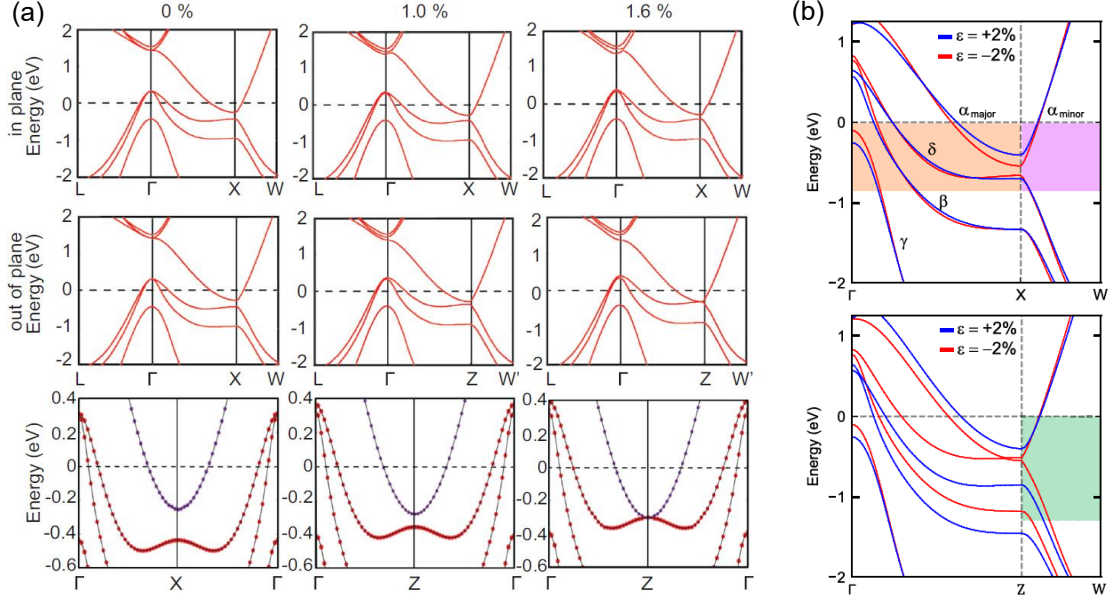


Figure 1.10: (a) Calculated band structures of LaSb with indicated compressed strain of 0 %, 1 % and 1.6 % [47]. (b) Calculated band structures of GdSb with 2 % of compressive (red) and tensile (blue) strain [48].

thin-film sample.

As shown in Fig. 1.10 (a), while the ground state of LaSb is a trivial semimetal, a compressive epitaxial strain of 1.6 % makes the La 5*d* and Sb 5*p* band cross near the Z point (the X point in the out-of-plane direction in rock salt structured *RESb* without biaxial strain), suggesting the appearance of a topologically nontrivial state [47]. Similarly, in GdSb, 2 % of compressive and tensile epitaxial strain results in nontrivial and trivial band topology, respectively, as shown in Fig. 1.10.

Considering that the lattice parameters of III-V semiconductors can be continuously varied by forming ternary compounds with precisely controlled composition, introducing biaxial strain of several percent is feasible. For example, ± 2 % strain for GdSb could be provided by $\text{Ga}_x\text{In}_{1-x}\text{Sb}$ buffer layer. Although this epitaxial strain-induced trivial to nontrivial topology transition has not been experimentally demonstrated yet, the reduction of the band gap at the Z point of GdSb was observed when compressive strain is applied [48]. This suggests the opportunities to investigate the interaction between magnetic order or magnetotransport properties and the band topology in *RESb* by fabricating and examining the same *RESb* material whose band topology is controlled by biaxial strain.

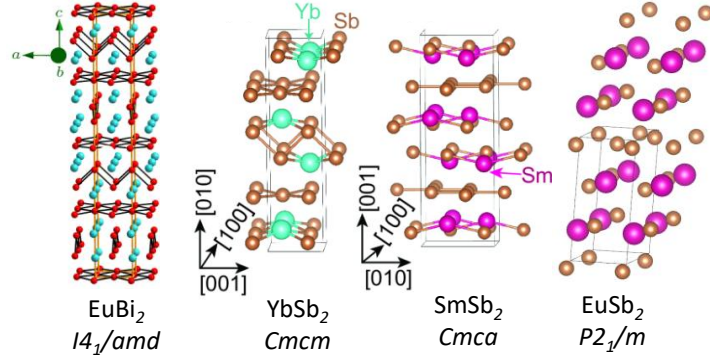


Figure 1.11: Typical crystal structures of $REPn_2$ [50–52].

1.1.2.2 Rare-earth dipnictides

Rare-earth dipnictides ($REPn_2$) are also common in $RE-Pn$ systems, except for rare-earth nitrides where only REN phases exist. Unlike the simple rock salt structure of $REPns$, $REPn_2s$ adopt more complex crystal structures with larger unit cells. Meanwhile, the crystal structures of $REPn_2s$ vary with composition.

As shown in Fig. 1.11, $REPn_2s$ exhibit layered structures consisting of $RE-Pn$ bilayers sandwiched by Pn sheets. $EuBi_2$ is crystallized in a tetragonal structure (space group $I4_1/amd$) [50], which is the highest-symmetrical structure in $REPn_2s$. On the other hand, many other $REPn_2s$ crystallize in an orthorhombic structure. While $YbSb_2$ [51, 53, 54] and $YbBi_2$ [55] are crystallized in structure with space group $Cmcm$, many light rare-earth ditanimonides such as $SmSb_2$ [56], $NdSb_2$ [57], $CeSb_2$ [58] and $LaSb_2$ [59] are crystallized in a slightly different structure with space group $Cmca$. Furthermore, $EuSb_2$ is crystallized in an even less symmetrical monoclinic $P2_1/m$ structure [52].

Many $REPn_2$ members, including $LaSb_2$, $EuSb_2$, $YbSb_2$, and $YbBi_2$, are reported to be nodal-line semimetals by first-principles calculations as well as experimental studies [51–53, 55, 59], despite their different crystal structure, while other $REPn_2$ members are also expected to share similar topological electronic states.

Because of the complex structural and topological electronic characteristics, $REPn_2s$ exhibit a diversity of exotic physical properties, which have attracted much attention in the past few years. For example, the anisotropic angle-dependent magnetoresistance and non-linear Hall effect in $EuSb_2$, $NdSb_2$, $YbSb_2$, and $YbBi_2$ [51–53, 57], the complex magnetic ordering with multiple magnetic transitions in $CeSb_2$ and $EuBi_2$ [50, 58], the non-saturate

linear magnetoresistance in LaSb_2 , NdSb_2 and epitaxial thin film of YbSb_2 [51, 57, 60], and the pressure induced structural transition in SmSb_2 and CeSb_2 [56, 61].

MBE growth of single-crystal thin-film $\text{RE}Pn_2\text{s}$ has been increasingly in the spotlight in very recent years [51, 52, 62, 63]. While epitaxial EuSb_2 thin film grown on $\text{Al}_2\text{O}_3(1120)$ exhibits the same crystal structure as the bulk material [52], other reports on epitaxial $\text{RE}Pn_2$ thin films indicate that the epitaxial thin films of $\text{RE}Pn_2\text{s}$ could adopt different structural characteristics and thus possibly show different physical properties compared with their bulk samples.

For example, epitaxial $\text{YbSb}_2(010)$ thin film grown on $\text{GaSb}(001)$ substrate holds a (2×1) surface reconstruction, although it still crystallizes in $Cmcm$ structure like bulk YbSb_2 [51]. while LaSb_2 and SmSb_2 thin films grown on $\text{MgO}(100)$ substrate exhibit a monoclinic structure formed with a different stacking mode of layers of YbSb_2 -like structure, rather than the orthorhombic structure of their bulk samples [62, 63]. These facts suggest that controlling the crystalline structure and, consequently, the physical properties of epitaxial $\text{RE}Pn_2$ thin films by using substrates with different lattice parameters and/or different in-plane rotational symmetry is possible.

1.1.2.3 Rare-earth pnictides in rare-earth-rich phases

For RE elements that can take more than one valence state, i.e., Eu , Yb , and Sm that can take both divalent and trivalent, and Ce that can take both trivalent and tetravalent, various RE -rich multi-rare-earth pnictide compounds could be formed in addition to $\text{RE}Pn$ and $\text{RE}Pn_2$, which exhibit even more diverse crystal structures as well as physical properties.

For example, Ce_2Sb and Ce_2Bi crystalized in $I4/mmm$ tetragonal structure, are reported to be heavy-fermion antiferromagnets with a tricritical point, where the transition between the antiferromagnetic ground state and magnetic-field induced phase changes from a first-order transition at low temperatures to a second-order transition at higher temperatures.[64]. Hexagonal Eu_5Bi_3 (space group: $P6_3/mcm$) is theoretically predicted to be a ferromagnetic Weyl semimetal with coexistence of both zero-dimensional Weyl points and one-dimensional Weyl nodal line [65]. Meanwhile, in cubic Yb_4As_3 , Yb_4Sb_3 and Yb_4Bi_3 (space group: $I\bar{4}3d$), valence fluctuation of Yb ions was observed [66, 67].

1.1.3 Ytterbium mononitride

Early reports on ytterbium mononitride (YbN) date back to the 1950s [68]. Like other *RENs*, YbN adopts the fcc rocksalt crystal structure and has the second smallest lattice parameter of 4.7852 Å within the *REN* family. As shown in Table 1.2, the *REN* family is ferromagnetic-dominated, while YbN is the only member showing an antiferromagnetic ground state with a bulk Néel temperature 0.79 K, which makes YbN special compared to other members. In early studies, YbN was considered a self-compensated semimetal, and the (semi-)metallic behavior was inferred from experimental results on bulk YbN crystals [69]. Meanwhile, the coexistence of both trivalent and divalent Yb ions in YbN has also been reported by a spectroscopic study on bulk YbN [70]. Similar to other *RENs*, early YbN bulk samples often also suffered from material issues, such as off-stoichiometry [70], which has been discussed as one of the possible origins of the observed metallic behavior or the mixed-valence Yb ions.

In recent years, MBE growth of *RENs* has enabled the fabrication of high-quality single-crystal *REN* thin-film samples, which have helped reveal the intrinsic properties of many *REN* members. However, studies on YbN thin films are very limited, due to the need for an activated nitrogen source for their growth, as Yb is incapable of catalyzing the dissociation of nitrogen molecules. So far, only two studies on the growth of YbN thin films have been reported.

Warring *et.al.* reported the synthesis of polycrystalline YbN thin films with (111) orientation on Al₂O₃ (0001) substrates by MBE using a Kaufman-type ion source [71]. From the x-ray absorption spectrum of Yb *M*-edge, as shown in Fig. 1.12 (a), only a peak corresponding to Yb³⁺ was observed, from which a completely trivalent state of Yb ions, which is different from the results on early bulk samples, was suggested. Meanwhile, from optical reflection and transmission measurements shown in Fig. 1.12 (b), the absorption edge was observed at approximately 1.5 eV, indicating that YbN is a semiconductor rather than a semimetal.

More recently, Loyal *et.al.* report another synthesis of YbN(111) thin films on MgO(100) and Al₂O₃(0001) substrates by magnetron sputtering [72]. As with the MBE-grown results mentioned above, semiconducting behavior of YbN was also observed. As shown in Fig. 1.13 (a), the real part of the dielectric function ϵ' shows the maximum at around 628 nm, indicating a band gap of around 2 eV. On the other hand, from the x-ray photoelectron

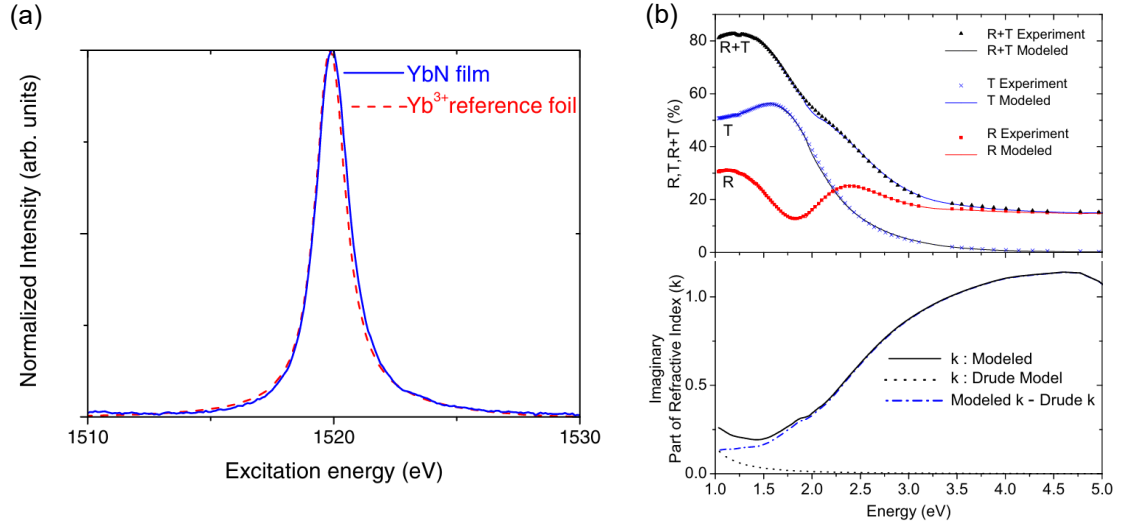


Figure 1.12: (a) *M*-edge x-ray absorption spectra of a YbN polycrystalline thin film grown by MBE with Kaufman-type ion source and Yb³⁺ reference film. (b) measured reflectance and transmittance from optical reflection and transmission measurements for a YbN film (upper), and the derived refractive index (lower) [71].

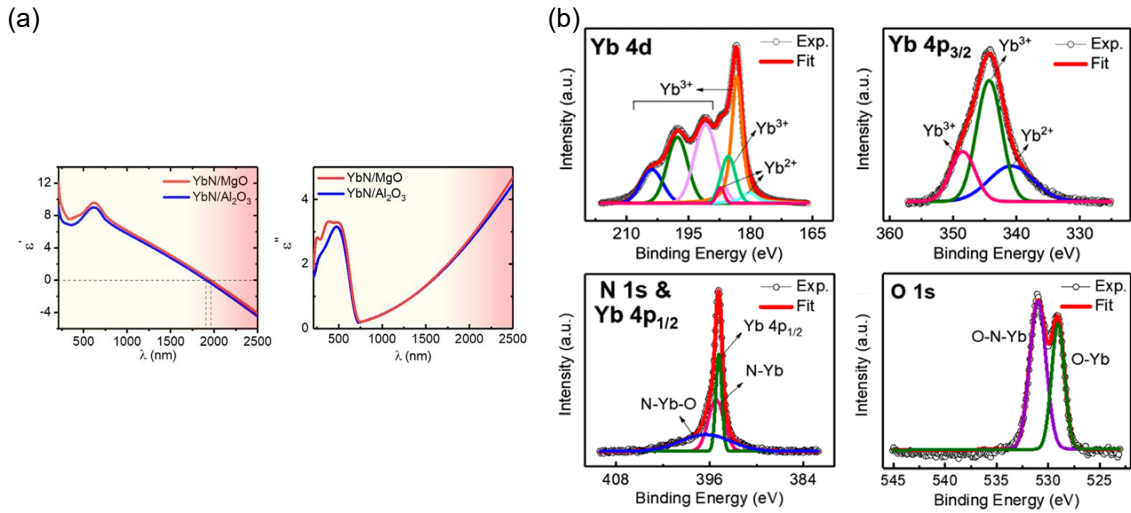


Figure 1.13: (a) Real (ϵ') and imaginary (ϵ'') part of the dielectric function of YbN thin films grown by magnetron sputtering. (b) core-level spectra measured by x-ray photoelectron spectroscopy [72].

Table 1.4: Crystal structure data of the Sb–Yb system extracted from Ref. [77].

Phase	Composition (at.% Yb)	Pearson symbol	Space group	Strukturbericht	Prototype
(Sb)	0	hR2	$R\bar{3}m$	A7	α As
Sb ₂ Yb	33.3	oC12	Cmcm	C49	ZrSi ₂
SbYb	50	cF8	$Fm\bar{3}m$	B1	NaCl
Sb ₁₀ Yb ₁₁	52.4	tI84	$I4/mmm$	–	–
Sb ₃ Yb ₄	57.1	cI28	$I\bar{4}3d$	D73	Th ₃ P ₄
β -Sb ₃ Yb ₅	62.5	hP16	$P6_3/mcm$	D88	Mn ₅ Si ₃
α -Sb ₃ Yb ₅	62.5	oP32	Pnma	–	–
(γ Yb)	100	cI2	$Im\bar{3}m$	A2	W
(β Yb)	100	cF4	$Fm\bar{3}m$	A1	Cu
(α Yb)	100	hP2	$P6_3/mmc$	A3	Mg

spectroscopy, evidence of the existence of both Yb²⁺ and Yb³⁺ is observed, as shown in Fig. 1.13 (b). Also, a significant oxygen content was observed.

The above-mentioned previous experimental reports on both early bulk and recent thin-film samples of YbN yield controversial results on two fundamental questions: whether YbN is a semiconductor or (semi)metal, and whether Yb ions in YbN are in a completely trivalent or a mixed-valence state. Meanwhile, for the reported thin-film samples, the material issues, i.e., partial oxidation, polycrystallinity, and the inherent instability of the polarized (111) growth orientation [73–76], remain unresolved. Therefore, the synthesis of high-quality single-crystal thin-film samples is still required to draw a decisive conclusion on the intrinsic properties of YbN.

1.1.4 Ytterbium antimonides

Unlike rare-earth antimonides with *RE* elements that usually only adopt trivalent, the Ytterbium antimonide (Yb-Sb) family includes many members with different Yb/Sb ratios. As shown in Table 1.4, in addition to the most common 1: 1 ytterbium monoantimonide (YbSb) phase and the 1: 2 ytterbium diantimonide (YbSb₂) phases that are also observed in other *RE*-Sb systems [78, 79], Yb-Sb compounds show more Yb-rich phases including Yb₁₁Sb₁₀, Yb₄Sb₃, and Yb₅Sb₃ [77]. Also, like Eu and Sm, Yb performs not only Yb³⁺, but also Yb²⁺ states when forming compounds. These facts make the study on ytterbium antimonides, especially the fabrication of the high-quality samples, much more complicated.

YbSb₂ is the Yb-Sb compound that attracted most attention in the past few years. As shown in Fig. 1.14 (a), YbSb₂ is crystalized in ZrSi₂-type orthorhombic structure (*Cmcm*),

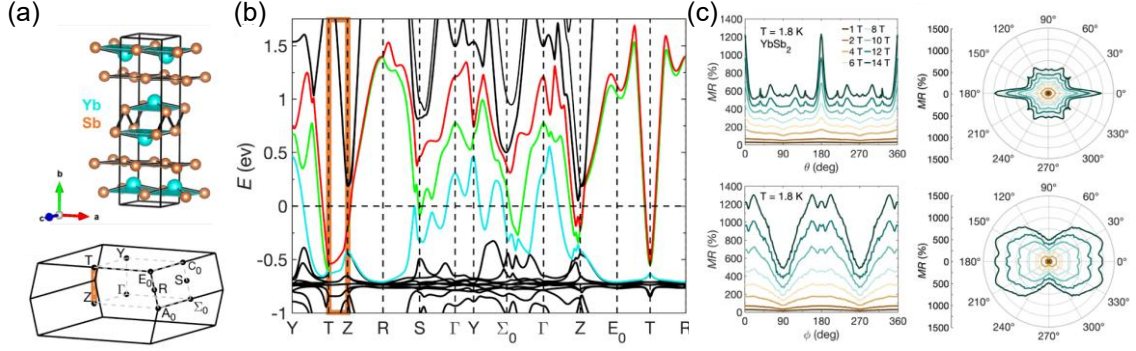


Figure 1.14: (a) Crystal structure and first Brillouin zone of YbSb₂. (b) Electronic structure of YbSb₂ acquired from DFT calculation. (c) Anisotropic magnetoresistance of YbSb₂ in ab plane (upper) and bc plane (lower) [53].

whose lattice parameters are $a = 4.561$ Å, $b = 16.72$ Å, and $c = 4.268$ Å [80]. From the density functional theory (DFT) calculations (Fig. 1.14 (b)) and quantum oscillation measurements [53, 80], it is indicated that YbSb₂ is a semimetal with a Dirac nodal line on the T-Z line.

For bulk YbSb₂, an angle-dependent anisotropic magnetoresistance was observed, as shown in Fig. 1.14 (c) [53]. Also, type-I superconducting state with a critical temperature of approximately 1.3 K has also been reported [81, 82].

In the meantime, YbSb₂ is the only member in the Yb-Sb family with the epitaxial thin-film sample reported [51, 83]. As shown in Fig. 1.15 (a) and (b), YbSb₂ epitaxial layers with (010) orientation can grow on GaSb(001) substrates with 45° in-plane rotation and form a (2×1) surface reconstruction. Meanwhile, YbSb₂ epitaxial thin film exhibits properties that differ from those in bulk form. While bulk YbSb₂ has been classified as a type-I superconductor, YbSb₂ thin film has been found to be in a mixed state of type-I and type-II superconductor with critical temperature and critical magnetic field of 1.025 K and 83.85 Oe, respectively. Also, different from the quadratic magnetoresistance behavior observed in bulk YbSb₂, linear non-saturating magnetoresistance has also been observed in YbSb₂ epitaxial thin film, as shown in Fig. 1.15 (c). In addition, a non-linear Hall effect was also observed [51].

While the origin of the non-linear Hall effect is attributed to the coexistence of both electron- and hole-like carriers because of the semimetallic nature of YbSb₂, the linear non-saturating magnetoresistance effect is considered to correspond to the complex and possibly topological electronic band structure with Dirac nodal line, as shown in Fig. 1.14. Therefore,

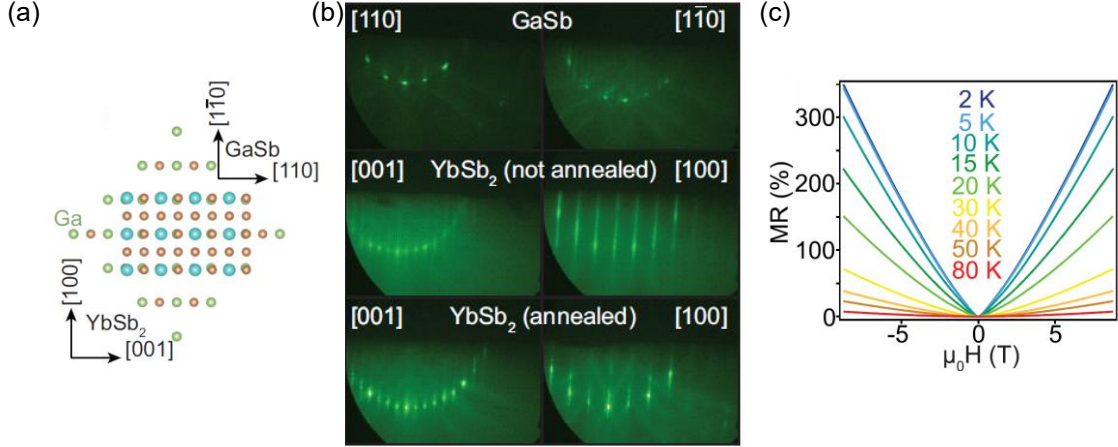


Figure 1.15: (a) Epitaxial relationship of GaSb(001) substrate and YbSb₂ layers. (b) RHEED patterns of GaSb(001) substrate and the YbSb₂ epitaxial layers. (c) Linear non-saturating magnetoresistance in YbSb₂ [51].

the experimental observation of the band electronic states of epitaxial YbSb₂ thin films by angle-resolved photoelectron spectroscopy is desirable to understand the relationship between the electronic structure and the observed transport properties under a magnetic field, as well as the differences between bulk and thin-film samples.

YbSb is another Yb-Sb compound that attracted research interests for several decades. Like other *RESBs*, YbSb is crystallized in the fcc rock salt structure, with the lattice parameter of 6.079 Å [84], and shows semimetallic behavior [85]. From early theoretical studies [86] as well as experimental studies using nuclear magnetic resonance [87, 88] and specific heat measurements [86] on YbSb powder samples, an antiferromagnetic ground state with a Néel temperature of around 0.5 K is suggested. Meanwhile, as shown in Fig. 1.16, there is another phase transition at approximately 5 K above the Néel temperature, which has been discussed to correspond to the formation of a mixing-type antiferroquadrupolar (AFQ) ordering.

However, there are no reports of a stoichiometric bulk single-crystal sample of YbSb, which has hindered further investigation of the electronic structure, transport properties, and the details of the phase transition associated with AFQ ordering. The difficulty of the fabrication of high-quality YbSb bulk samples is considered to originate from the high vapor pressure of Yb [89], and the easy formation of Yb₁₁Sb₁₀ impurities [85].

Given the good lattice matching ($\Delta a \approx +0.2\%$) between GaSb ($a = 6.096$ Å) and YbSb ($a = 6.081$ Å) [84], MBE growth of single-crystal YbSb thin films is expected to be the

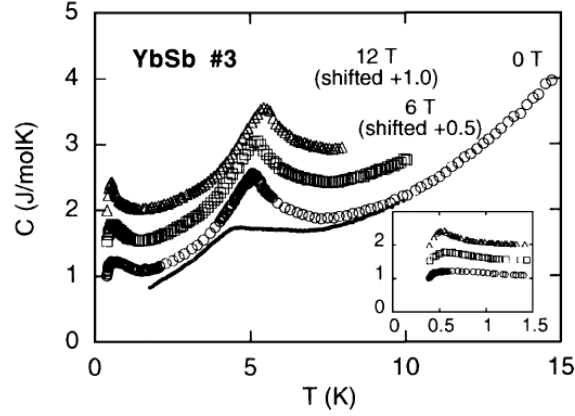


Figure 1.16: Temperature dependence of the specific heat for a YbN powder sample [86].

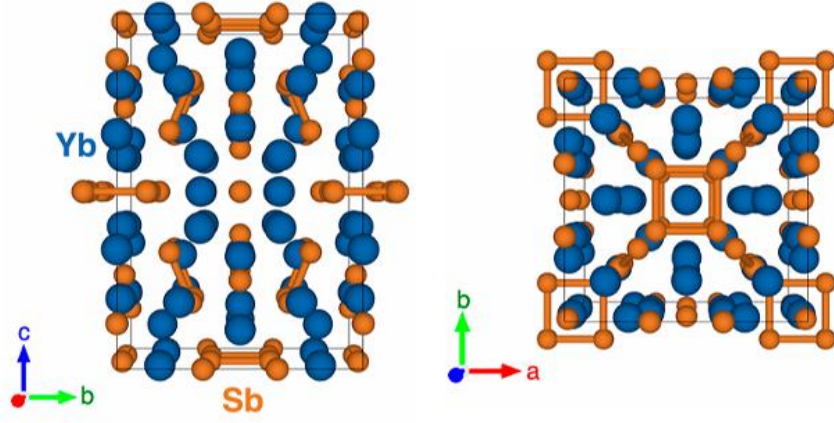


Figure 1.17: Crystal structure of $\text{Yb}_{11}\text{Sb}_{10}$ [90].

possible approach to investigating the fundamental properties, such as the electronic band structure of YbSb.

For Yb-rich Yb-Sb compounds, $\text{Yb}_{11}\text{Sb}_{10}$ crystallize in a more complicated tetragonal structure (space group: $I4/mmm$) with a large unit cell ($a = b = 11.86 \text{ \AA}$, $c = 17.10 \text{ \AA}$), as shown in Fig. 1.17 [90–93]. This leads to the low lattice thermal conductivity, making $\text{Yb}_{11}\text{Sb}_{10}$ a structurally ideal base material for thermoelectric properties, while doping other elements such as Mn, Cr, and Ge into the system has been confirmed to be effective to achieve a high Seebeck coefficient for thermoelectric applications [90, 93]. Meanwhile, Yb_4Sb_3 was reported to be a valence fluctuation material [66], while Yb_5Sb_3 was theoretically predicted to be a promising candidate of Mott-insulating electrifieds [94]. MBE growth of single-crystal thin films of these Yb-rich phases is expected to facilitate detailed inves-

tigation of their structural and electronic properties, as well as further studies of potential applications.

1.2 Purpose of this study

In this study, we focused on the opportunity to reveal the structural and electronic properties of YbN and Yb-Sb compounds, using the MBE-grown single-crystal thin-film samples. The specific purposes are as follows:

For YbN with controversial reports on (semi)metallic/semimetallic nature and Yb valence state because of the material issues of both bulk and thin-film samples reported so far, we attempted to fabricate high-quality stoichiometric and epitaxial YbN(100) thin films by MBE assisted by nitrogen plasma source, and then to determine the structural characteristics and electronic structure, especially the band gap and the Yb valence state, with a combination of electron/x-ray diffraction and photoelectron spectroscopy.

For Yb-Sb compounds, we directly observed the electronic band structure of YbSb₂ epitaxial thin film with ARPES to investigate the origin of their special transport properties under a magnetic field. Meanwhile, we carefully conducted an MBE growth study on Yb-Sb thin films to determine whether single-crystal Yb-Sb thin films with other Yb/Sb ratios, especially YbSb, could be synthesized.

Chapter 2

Experimental methods

This chapter outlines the experimental methods employed in this study.

The general flow of the experiment in this study is shown in Fig. 2.1. The thin-film samples were prepared by molecular beam epitaxy (MBE). For each fabricated thin film, the surface atomic structure was monitored by electron diffraction, including reflection high-energy electron diffraction (RHEED), and the electronic structure was measured by photoelectron spectroscopy (PES). The above-mentioned procedures were conducted continuously over the course of one day in an ultra-high vacuum (UHV) environment. Meanwhile, the observed results were used as feedback, which helped investigate the dependence of growth on each growth parameter and optimize the growth conditions. Typical samples that need further investigation of the detailed crystal structure would be capped with Cr metal before being removed from the UHV system, and then an *ex situ* x-ray diffraction (XRD) measurement would be conducted. The experimental methods used in this study will be introduced in the following sections.

2.1 Molecular Beam Epitaxy [95, 96]

Molecular beam epitaxy (MBE) is a physical vapor deposition method for thin-film growth. It could be considered as an extension or development of thermal evaporation [97]. Still, with a cleaner environment in the ultra-high vacuum (UHV) system, well-controlled moderate deposition and growth rate, resulting in the capability to fabricate thin-film samples with high crystallinity, minor impurities, perfect stoichiometry, and smooth surface/interfaces.

These advantages of MBE make it not only a effective method to synthesize high-quality samples for the fundamental studies on physical properties of the materials, but also the

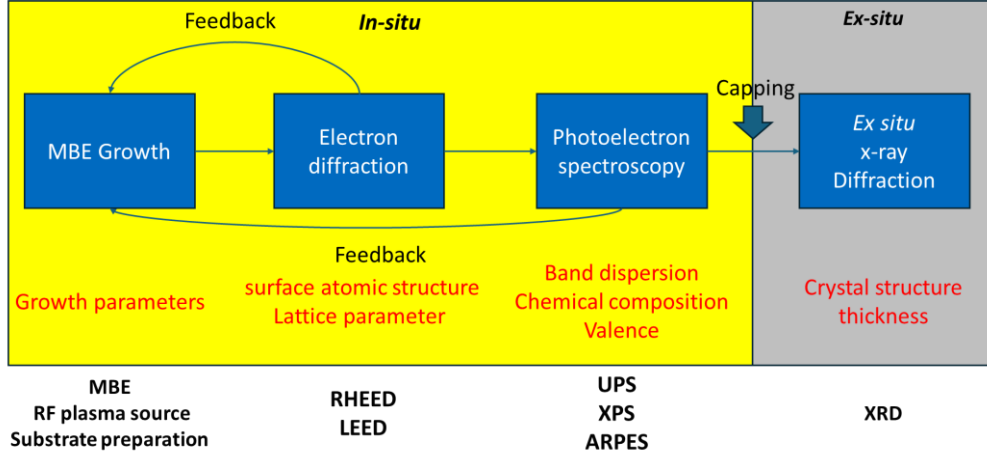


Figure 2.1: General flow of the experiment in this study.

promising candidate for the manufacture of a wide range of technologies, such as photovoltaic semiconductor devices [98], metal-oxide semiconductor field-effect transistors (MOS-FETs) [99], micro- and nano-electromechanical systems (MEMs and NEMS) devices [100], and magnetic storage media [101], because many of their properties depend strongly on the quality of surface and interfaces.

In this section, the general experimental setup of an MBE system is described, along with the operating principles and mechanisms of each component.

2.1.1 Typical MBE setup

Figure 2.2 schematically illustrates the typical setup of an MBE system. In general, an MBE system should include the following components: UHV chambers and a pumping system, evaporation sources, a substrate holder with heating and manipulation capabilities, and an *in situ* monitoring or characterizing system.

2.1.2 Ultra-high vacuum (UHV) system

The pumping and sealing systems that maintain the UHV environment are essential for the MBE growth. A UHV environment could significantly increase the mean free path of evaporated atoms or molecules, enabling them to travel from the evaporators to the substrate without collision. Meanwhile, the UHV environment also minimizes the adsorption of impurity atoms on the substrate or sample surface and prevents potential reactions with

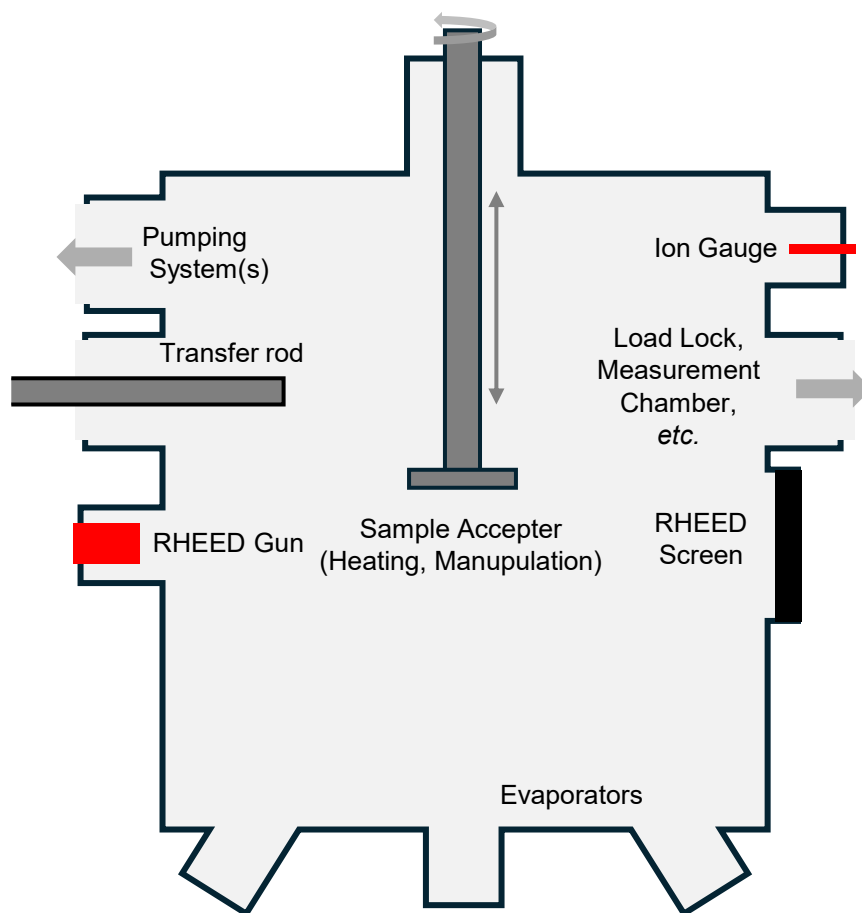


Figure 2.2: Schematic illustration of a typical MBE setup.

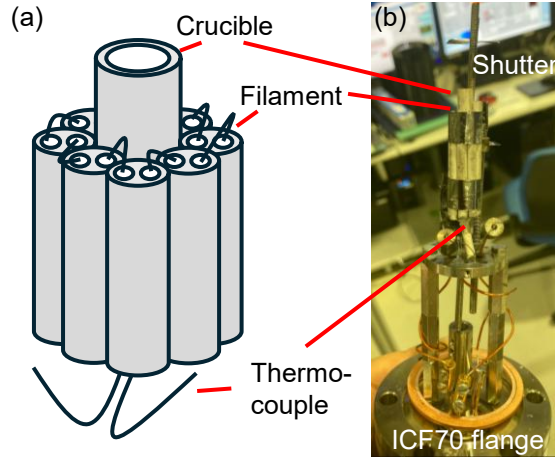


Figure 2.3: (a) Schematic illustration of a simple design of the K-cell. (b) a K-cell which is made based on the design in (a).

residual gases, especially for materials that are easily oxidized or hydrated, such as rare-earth elements. These facts minimize contamination and facilitate the growth of films with atomically smooth and clean surfaces.

Usually, the ultra-high vacuum environment with a base pressure better than 1×10^{-7} Pa (or samely 1×10^{-9} mbar) is maintained by a turbo molecular pump. To reach a lower pressure, or to exclude the influence of the residual gases that are difficult to pump out by the turbo molecular pump, such as water, hydrogen, and noble gases, getter pumps, such as a titanium sublimation pump [102] or a cryopump [103] will be used together with the turbo molecular pump.

2.1.3 Knudsen-type effusion cell (K-cell) [104, 105]

Knudsen-type effusion cell (K-cell) is the most widely used evaporation source in MBE growth of thin films, because of its excellent flux stability, simple and robust design, broad compatibility with various kinds of materials (without extremely high evaporation temperature, wetting, or reactions with the crucible), and predictable effusion behavior by the vapor-pressure model.

The minimum components of a K-cell are extremely simple: a crucible that holds the source material, a heating system such as a tungsten filament that thermally evaporates the material, and a set of thermocouples for temperature measurement and closed-loop temperature control, if needed. This makes K-cells reliable MBE sources that are easily

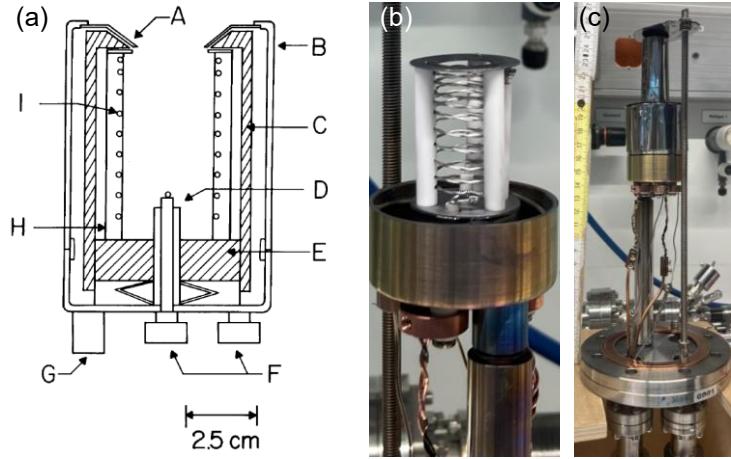


Figure 2.4: (a) Radak II oven for the K-cell, consists of molybdenum vapor shield (A), stainless steel cover (B), multilayer tantalum radiation baffle (C), spring-loaded thermocouple (D), tantalum radiation baffle (E), terminal connectors(F), mounting post (G), alumina heater supports (H), and tungsten heating filament (I) [104]. (b-c) Photos of a Radak II K-cell. (b) Inner structure of the Radak II oven. (c) A constructed a K-cell with a handmade collimator and shutter.

accessible and budget-friendly.

Figure 2.3 (a) shows the schematic picture of a simple design for a handmade K-cell, which contains only tungsten wires, alumina insulative tubes, and a set of thermocouples. A photo of one of the handmade K-cells based on this design is shown in Fig. 2.3 (b), which is mounted on an ICF70 UHV flange, together with a shutter to control the start and stop of the delivery of the flux of substrate. This simple structure is proven to be reliable enough to provide stable flux around $1 \text{ \AA}/\text{min}$ with $0.1 \text{ \AA}/\text{min}$ accuracy while maintaining the pressure in the MBE system at around $1 \times 10^{-7} \text{ Pa}$, for the materials with relatively low evaporation temperature, such as ytterbium and antimony, which evaporate at around 400°C .

More delicately designed and constructed commercial K-cells exhibit better performance in reaching temperature, power efficiency, and outgassing suppression. A typical Radak II K-cell from Luxel Corporation is shown in Fig. 2.4 [104]. As shown in Fig. 2.4 (a), when a crucible is set in the Radak II furnace, the spring-loaded thermocouple (D) ensures that the top of the crucible presses against the molybdenum vapor shield (A), which prevents the evaporated material from entering the inner spaces of the oven and forming contamination. This enables the flexible use of a single K-cell for different materials by simply changing only the crucible and vapor shield, while keeping the major parts unchanged. Meanwhile,

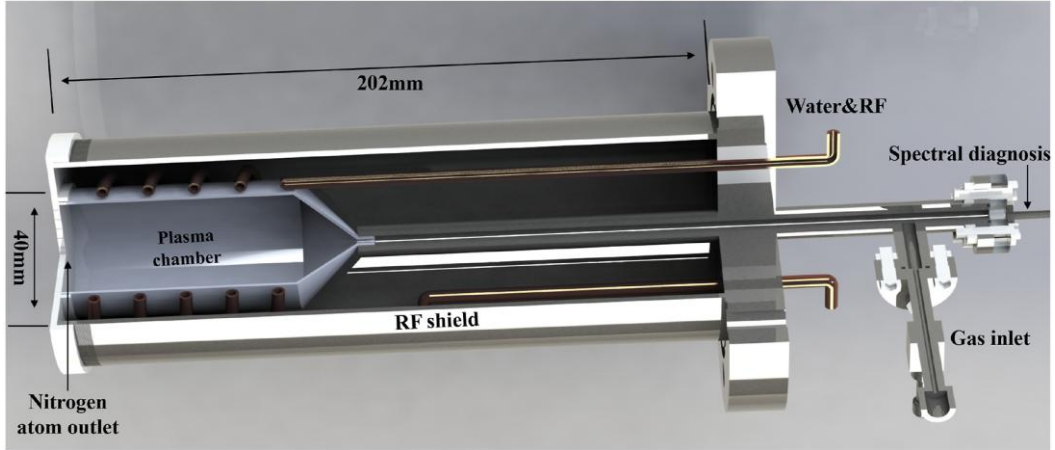


Figure 2.5: schematic of RF nitrogen plasma source [108]

the filament and crucible are surrounded by the tantalum radiation baffle (C and E), which forms an almost isothermal enclosure, minimizing heat loss. This not only improves power efficiency but also reduces chamber heating and the heating of elements around the effusion cell, resulting in a higher deposition temperature and less outgassing during deposition.

Commonly, the above-mentioned designs enable us to evaporate materials at around 1000 °C, while maintaining a pressure within the 10^{-8} - 10^{-7} Pa range during deposition. Special-designed K-cells with water-cooling systems can reach even higher temperatures of up to 2000 °C, further extending the potential of MBE growth using K-cells. However, one should be aware that the choice of crucible materials would be very limited at such high temperatures.

2.1.4 Radiofrequency (RF) plasma nitrogen source [106–108]

Plasma-assisted MBE with nitrogen supplied from radiofrequency (RF) nitrogen plasma sources is commonly used for the growth of III-nitride thin films. Compared with other common nitrogen ion sources, such as electron cyclotron resonance (ECR) plasma sources [109], Kaufman ion sources [110], and microwave ion sources [111], the RF plasma source operates at a lower temperature and provides more neutral nitrogen atoms and fewer low-energy nitrogen ions [112]. This suppresses surface damage during thin-film growth and facilitates epitaxial growth.

The RF plasma source, schematically illustrated in Fig. 2.5, operates by using radio-frequency electromagnetic fields to dissociate and ionize the nitrogen molecules continuously.

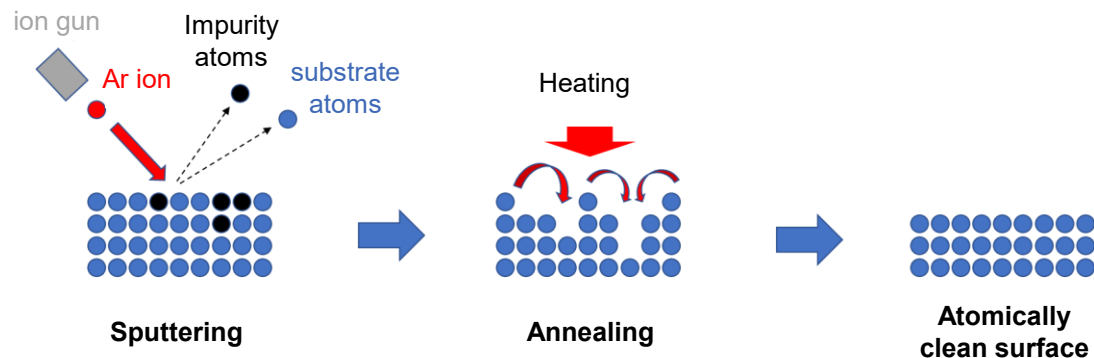


Figure 2.6: Schematic illustration of the sputter-anneal method.

High-purity nitrogen is introduced into the plasma chamber from a nitrogen flow meter or a variable leak valve. An RF current, typically 13.56 MHz, is applied to the coil wrapped around the plasma chamber. The time-varying RF current generates a magnetic field inside the plasma chamber, which, according to Faraday's law, induces an oscillating electric field. The oscillating electric field that drives electrons moving back and forth in the chamber, and the electrons collide with the supplied nitrogen molecules to form various active nitrogen species, including neutral radicals N and N*, together with some ions like N_2^+ or N^+ . During the process, more electrons and ions are created. When the number of moving electrons and ions reaches a threshold, the plasma will ignite, and a large amount of radical nitrogen will be continuously supplied by the RF plasma source.

2.1.5 Substrate preparation

In this study, two types of substrates were mainly used: oxide substrates, including MgO(100), LaAlO₃(100), and YVO₄(100), and GaSb(110) and GaSb(001) semiconductor wafers.

Different cleaning methods were applied to the two substrates to achieve atomically clean and flat surfaces for the epitaxial growth of thin-film samples. For oxide substrates, heating (annealing) in an oxygen atmosphere was performed to remove surface carbon residuals.

On the other hand, semiconductor wafers were cleaned by the sputter-anneal method, as shown in Fig. 2.6. In this method, the surface is first cleaned by argon ion sputtering, which physically removes contaminants and native oxides. Then, the substrate is subsequently annealed to restore the surface crystallinity and reconstruct the damaged top layers, utilizing

thermally activated atomic motion. By repeating the sputtering and annealing cycles, a well-ordered, contamination-free surface can be efficiently and reproducibly obtained. One should also keep in mind that the sputter-anneal method has its own limitations, such as changes in surface stoichiometry due to differences in sputtering yields among elements.

Meanwhile, since the (110) plane of zinc-blende-structured GaSb is a non-polar cleavage plane, the clean GaSb(110) surface was also prepared by cleaving a GaSb(001) wafer in the UHV chamber.

2.1.6 Quartz crystal thickness monitor [12]

A quartz crystal thickness monitor is a commonly used device in MBE systems for measuring the evaporator flux rate and estimating the approximate thickness of the synthesized thin film. (To get accurate thickness, other measurements such as RHEED oscillation or XRR are needed, which would be introduced in Section 2.1.7 and Section 2.3.2.4.)

Quartz crystal thickness monitor operates by detecting the changes in the resonance frequency of an AT-cut quartz crystal (quartz crystal cut at about 35° relative to the optical axis) subjected to shear mode oscillation during the deposition, and calculating the corresponding mass deposition (which could be easily converted into thickness when the deposited material is known), because of the stable piezoelectric response of quartz [113], when an alternating voltage is applied from the electrodes on the quartz crystal, a shear-mode vibration with a well-defined resonance frequency occurs.

When material is deposited onto the crystal surface from an effusion cell, the effective mass of the crystal oscillator increases, resulting in a decrease in the resonance frequency of the system.

Assuming that the layers deposited on the quartz crystal are rigid and uniform, the change in mass per unit area Δm is given by

$$\Delta m = \frac{c_q \rho_q}{2} (1/f_f - 1/f_q) \quad (2.1)$$

where c_q is the velocity of the transverse acoustic shear wave travelling in quartz crystal, ρ_q is the density of quartz, f_q and f_f are the resonant frequencies before and after deposition. Furthermore, if the deposited layer is thin enough compared with the acoustic wavelength in quartz crystal (approximately 1 mm assuming a typical acoustic velocity in solid of 3000 m/s

and a commonly used frequency of 5 MHz), equation 2.1 could be simplified as

$$\Delta m = \frac{c_q \rho_q}{2} \frac{\Delta f}{f_q^2} \quad (2.2)$$

where Δf is the frequency shift.

Given that the density ρ is usually known, the thickness of the layer that is deposited on the quartz crystal is given by

$$t = \Delta m / \rho = \frac{c_q \rho_q}{2\rho} \frac{\Delta f}{f_q^2} \quad (2.3)$$

The flux rate could be derived from the temporal development of t .

When the deposited layer on the crystal monitor is not acoustically negligible, for example, extremely thick layers are deposited on the crystal and the resonance frequency varies more than 5 % compared with the value before deposition, the correction of the Z-ratio is needed. The detailed introduction of the Z-correction will be omitted here.

2.1.7 Reflection high-energy electron diffraction (RHEED)[114]

Reflection high-energy electron diffraction (RHEED) provides an efficient, real-time way to monitor the surface atomic structure of substrates and thin films during MBE growth and is thus commonly incorporated into MBE systems.

A typical RHEED system consists of an electron gun to provide, focus, and manipulate high-energy electrons (10-20 keV), and a fluorescence screen together with a camera system on the opposite side of the RHEED gun to capture diffracted electrons. Typically, the MBE chamber alignment is designed to allow the incident electron beam to strike the sample surfaces at a glancing angle of several degrees at the growth position.

Figure 2.7 schematically illustrates the basic principle of the RHEED measurement.

When electrons with a wavevector of $\mathbf{k}_0$ incident on the surface of a single-crystal sample with perfect periodicity, considering only the elastic scattering, the wavevector of the diffracted electrons is given by

$$\mathbf{k} = \mathbf{k}_0 + \mathbf{G} \quad (2.4)$$

where $\mathbf{G}$ is a reciprocal lattice vector. Here, the magnitudes of the wavevector $\mathbf{k}_0$ and $\mathbf{k}$ are the same, or in another words, $\mathbf{k}$ share the same start point with $\mathbf{k}_0$, and it end points are on the sphere with a radius of $|\mathbf{k}_0|$, which is well-known as the Ewald's sphere. Therefore, the diffractions appear at the direction where reciprocal lattice points meet the Ewald's

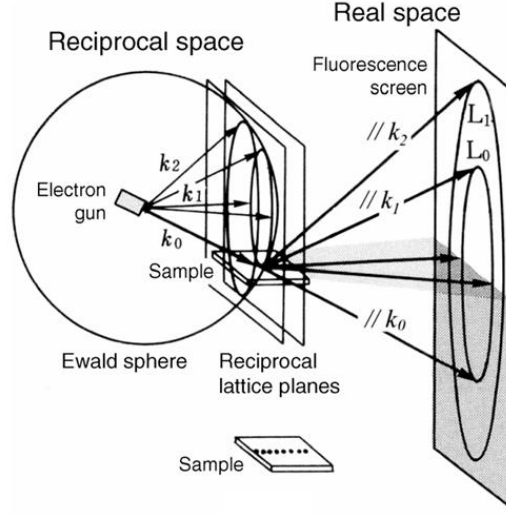


Figure 2.7: Schematic illustration of RHHED measurement in real and reciprocal space [114].

sphere. This is reflected in the RHEED measurement in real space by the pattern, where diffraction spots (streaks) with a certain horizontal spacing corresponding to the reciprocal lattice parameter appear in the directions at which the reciprocal lattice planes intersect the Ewald's sphere, forming a different set of ring-like structures.

From the spacing x of the diffraction spots or streaks, the surface lattice parameter in real space can be derived by

$$a = \frac{n\lambda\sqrt{x^2 + L^2}}{x} \quad (2.5)$$

where λ is the wavelength of the incident electron, and L is the distance between the measured point on the sample surface and the RHHED screen. If $x \ll L$, this can be further simplified as

$$a = \frac{n\lambda L}{x} \quad (2.6)$$

In MBE growth of thin film samples, since the lattice parameter of the substrate a_{sub} is usually already known, the surface lattice parameter can also be derived from

$$a_{film} = \frac{a_{sub}x_{sub}}{x_{film}} \quad (2.7)$$

which is more often used.

Besides calculating the lattice constant, another important role of the RHEED in an MBE system is to evaluate the crystalline quality of the substrate or sample surface. Figure

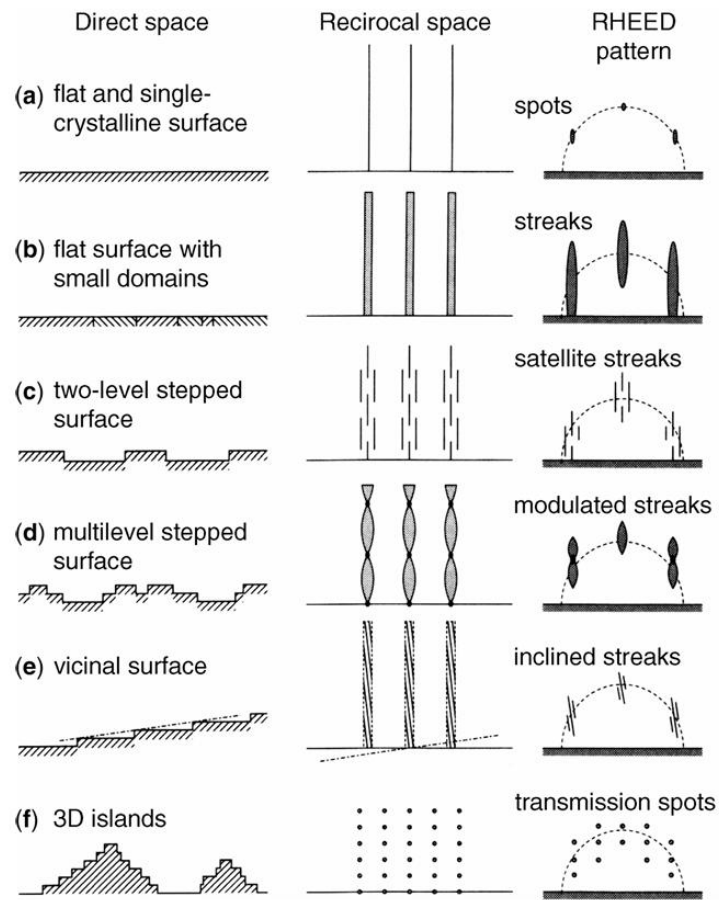


Figure 2.8: Schematic of the often-observed RHEED patterns, together with the corresponding surfaces in real space [114].

2.8 illustrates the RHEED patterns commonly observed together with the corresponding surfaces. For the surface of a perfect single-crystal sample, sharp spots on the rings would be observed by RHEED, as shown in Fig. 2.8 (a). However, this pattern is usually observed only on single-crystal substrates and is rarely realistic for most thin-film samples, since grain boundaries cannot be excluded even in well-controlled epitaxial growth. On a flat surface that consists of several domains with the same orientation, a streak-like feature will appear at the positions where spots appear in a perfect single crystal.

The flatness of the surface further modulates the shape of the RHEED pattern. For stepped surfaces, the streaks in the RHEED pattern will split into satellite streaks and form intensity-modulated streaks if there are multiple different levels on the surfaces, as shown in Figs. 2.8 (c) and 2.8 (d). For even more three-dimensional surfaces, i.e., a completely three-dimensional island-grown surface, transmission spots that evoke the reciprocal lattice would be observed.

The above-mentioned RHEED patterns correspond to surfaces with uniform orientation, regardless of domain size or three-dimensional structure. Surfaces consist of randomly oriented small domains; in other words, polycrystalline surfaces exhibit ring-like structures without spots or streaks. Furthermore, on amorphous surfaces, no structures can be observed, but the background intensity increases.

Real-time monitoring of thickness via RHEED intensity oscillation is another fact that makes RHEED irreplaceable in an MBE system.

Electrons diffracted to the same diffraction spot exhibit interference with each other. When electrons are reflected from a completely flat surface, the diffraction spots always exhibit enhanced intensity because of constructive interference, since there is no path difference for electrons reflected from the same atomic plane. In contrast, when the surface is not uniformly covered, the paths of electrons reflected from different atomic layers differ, leading to a deviation from constructive interference and, consequently, reduced diffraction spot intensity.

For the reason mentioned above, the periodic oscillation of RHEED intensity occurs. RHEED intensity oscillation is schematically shown in Fig. 2.9. Considering a layer-by-layer fashion of epitaxial growth, when one complete layer is formed, constructive interference occurs, and the intensity of the RHEED pattern reaches a maximum. As more atoms deposit onto the surface and a second layer begins to form, the intensity decreases due

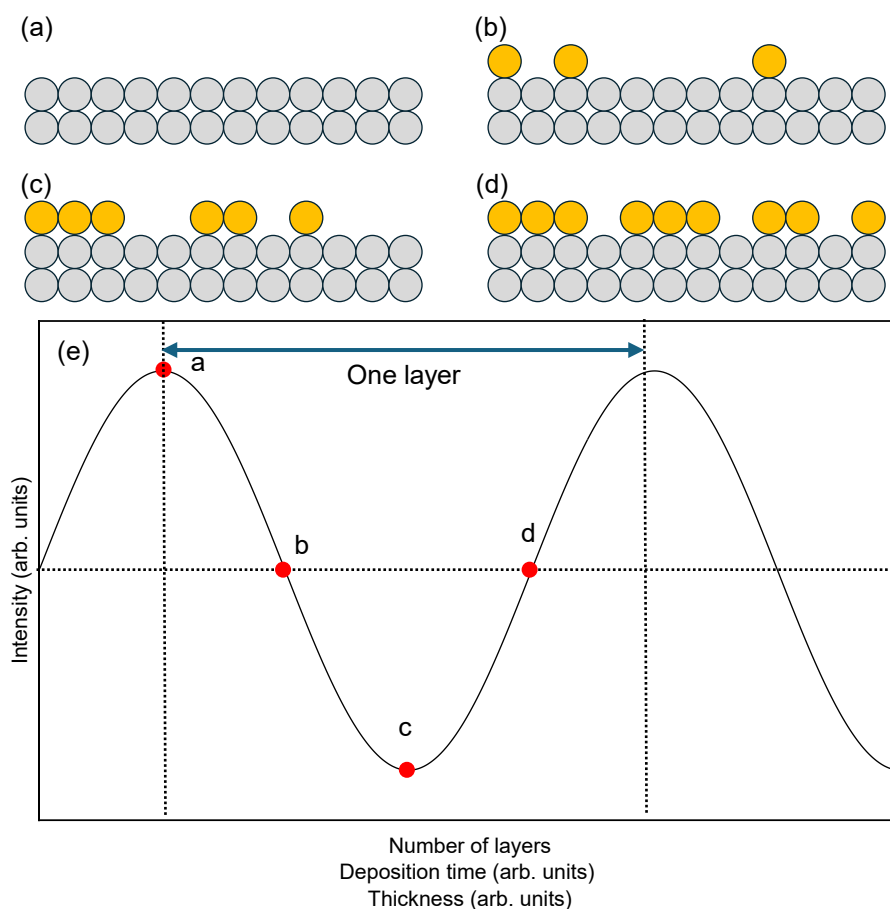


Figure 2.9: RHEED intensity oscillation

to a deviation from the constructive interference condition. The decrease in intensity will continue until the surface is half-covered, at which point the intensity reaches a minimum. The intensity will then increase again until a complete layer forms, and the cycle repeats. Therefore, the RHEED pattern shows periodic intensity oscillations with increasing layers, with maxima indicating the formation of a fully covered surface, and the oscillation period suggesting the time, thickness, or number of atoms deposited, which are needed to form 1 layer.

2.1.8 Low energy electron diffraction (LEED) [115]

Low-energy electron diffraction (LEED) is another useful tool for investigating the surface crystalline structure. In LEED measurements, electrons with kinetic energies typically ranging from several tens to several hundred eV are directed onto the sample surface in a normal incident. The electrons scattered by surface atoms produce diffraction patterns that reflect the surface atomic arrangement.

From the de Broglie relation, the wavelength λ of an electron is given by

$$\lambda = h/p \quad (2.8)$$

where h is Planck's constant and p is the momentum of the electron. Within the non-relativistic approximation, the kinetic energy of an electron can be expressed as

$$E_k = \frac{p^2}{2m} \quad (2.9)$$

where m is the mass of the electron. Combining the two equations above, the wavelength of the electron can be written as

$$\lambda = \frac{h}{\sqrt{2mE_k}} \approx \sqrt{\frac{1.504}{E_k}}(\text{nm}) \quad (2.10)$$

in which E_k is expressed in electron volts. Substituting the kinetic energy of 100 eV into equation 2.10, the wavelength can be calculated to be 0.12 nm, which is in the same order as the lattice parameters in common materials. This guarantees that the diffraction pattern reflecting the surface atomic arrangement can still be observed even for normal incidence in LEED measurement. Meanwhile, as shown later in Fig. 2.14, the inelastic mean free path, and thus the penetration depth of electrons with several tens to several hundreds eV, is smaller than 1 nm, ensuring the high surface sensitivity of LEED measurement.

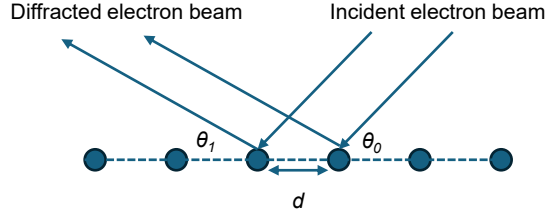


Figure 2.10: schematic illustration of the electron diffraction by a one-dimensional atomic row.

Considering the diffraction of a one-dimensional atomic row, as shown in Fig. 2.10, the condition of constructive interference is given by

$$d \cos \theta_0 - d \cos \theta_1 = n\lambda \quad (2.11)$$

where d is the atomic spacing, θ_0 and θ_1 are the incident and exitant angle of the electron beam, and n is an arbitrary integer. This condition can be further rewritten as

$$\frac{1}{\lambda} \cos \theta_0 - \frac{1}{\lambda} \cos \theta_1 = \frac{n}{d} \quad (2.12)$$

The diffracted electrons only appear in specific directions θ_1 that satisfy the above-mentioned relation. Therefore, by measuring the diffraction angles, the atomic spacing d can be determined. This can be extended to a two-dimensional case when adding symmetry and directional distribution information, from which the atomic periodicity of the sample surface can be derived.

Since electrons penetrate only the uppermost several layers of the material, the surface can be treated as a two-dimensional crystal for LEED measurements. In reciprocal space, the two-dimensional surface can be represented by reciprocal lattice rods extending perpendicular to the surface, because there is no periodicity, or in other words, the period is close to infinity, for the completely two-dimensional crystal. Therefore, the diffraction only occurs in the direction where Ewald's sphere with radius $1/\lambda$ (elastic process) intersects the reciprocal lattice rods spaced by $1/d$. Given the normal incidence condition ($\cos \theta_0 = 0$) of the typical LEED setup, the diffraction condition is simplified to be

$$\frac{1}{\lambda} \cos \theta_1 = \frac{n}{d} \quad (2.13)$$

The diffraction condition is schematically illustrated in Fig. 2.11.

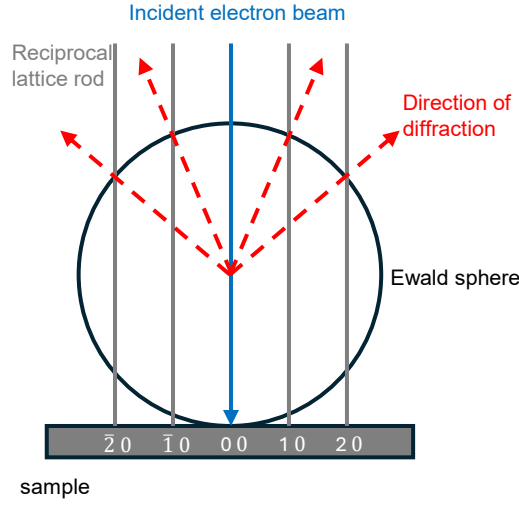


Figure 2.11: Schematic illustration of the direction where the diffraction patterns appear in LEED measurement.

2.1.9 Lattice mismatch

Epitaxial growth in MBE can be categorized into homoepitaxy and heteroepitaxy, depending on whether the film and the substrate consist of the same or different materials. Homoepitaxial growth is widely used in the substrate preparation process to achieve cleaner, more defect-free layers on the same material.

On the other hand, heteroepitaxy involves growing an epitaxial film on a substrate composed of a different material. In most situations, the lattice parameters of the substrate and the thin film are different, leading to lattice mismatch and the resulting strain.

Assuming that the lattice constant of the substrate and the film are a_s and a_f respectively, the lattice mismatch η , which expresses how much the natural lattice constant of the films differs from that of the substrate, is given by

$$\eta = \frac{a_s - a_f}{a_s} \quad (2.14)$$

In general, a smaller absolute value of the lattice mismatch indicates a higher possibility of growing high-quality epitaxial layers.

As shown in Fig. 2.12, by different lattice mismatches, the MBE growth could be divided into three different situations. $\eta = 0$ indicates perfect lattice matching, where no strain is introduced into the layers. When $\eta > 0$, or in other words, the substrate lattice constant is larger than that of the film, the film experiences tensile strain. On the other hand, when

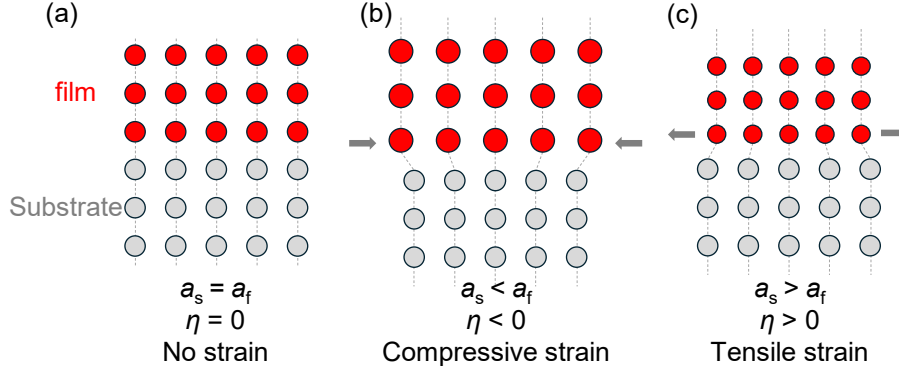


Figure 2.12: Schematic of the different situations depending on the relationship between the lattice parameters of the film and the substrate.

$\eta < 0$, the compressive strain is created in the film.

One should keep in mind that mismatch-induced uniform strain can usually be applied only to the first few layers grown on the substrate. When the thickness of the film increases beyond a critical thickness, the strain in the film will be relieved, and the lattice parameter, which is the same as the bulk value, can be observed in a film that is thick enough. This process is known as strain relaxation [116].

2.2 Photoelectron Spectroscopy (PES)

Photoelectron spectroscopy (PES) is a technique that probes the occupied electronic states of materials using the photoelectric effect. When light incident on the material, the electrons within the material gain energy from the photons and are excited to higher energy states. If the electrons gain enough energy and are excited to energy levels above the vacuum level, they can be emitted from the material surface. The emitted electrons (photoelectrons) are subsequently detected by an electron energy analyzer. By measuring the kinetic energy of the photoelectrons and applying the principle of energy conservation, the binding energies of the corresponding occupied states can be determined. Furthermore, by measuring photoelectron emission angles and accounting for momentum conservation, the dispersion of the occupied states in momentum space (i.e., band dispersion) can be directly obtained. Additionally, by adjusting the polarization of the incident light or incorporating a spin detector, it is also possible to extract information on the orbital symmetry and spin polarization of the occupied states.

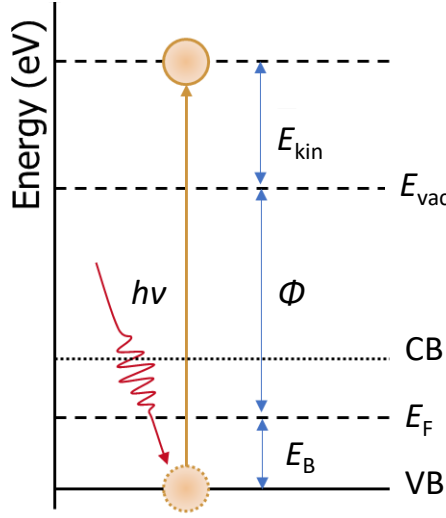


Figure 2.13: Schematic illustration of PES. VB, CB, E_F and E_{vac} denote the valence band, conduction band, Fermi level, and vacuum level, while E_B and ϕ are the binding energy (the energy difference of Fermi level and the chosen occupied state) and the work function (the energy difference between vacuum level and Fermi level.)

2.2.1 Basic Principles of the Photoelectron Spectroscopy [117]

The energy conservation during the photoemission process is schematically illustrated in Fig.2.13. When photons with energy $h\nu$ are incident on a material, electrons within the material may be excited to energy levels above the vacuum level if the photon energy is great enough. If this excitation occurs, the electrons can escape from the material as photoelectrons.

If we denote the initial and final energies of the electron before and after excitation as E_i and E_f , respectively. According to the law of energy conservation, the following relation can be derived:

$$E_{\text{kin}} = h\nu - \Phi - E_B \quad (2.15)$$

Since the photon energy $h\nu$ is usually a parameter that already known and the work function Φ is a constant for a given material, the binding energy E_B of the initial energy state can thus be calculated by detecting only the kinetic energy E_{kin} of the photoelectron using Eq. (2.15).

Furthermore, by accounting for factors such as the photoexcitation cross section, the photoelectron intensity provides information on the density of states (DOS) of the corresponding

occupied states.

Generally, it is easy to consider the process from incident light entering the materials to the emission of a photoelectron as three steps.

- 1) Excitation of the electrons in the material by gaining energy from the incident light, that is greater than the summation of the work function Φ of the material and the binding energy E_B , another energy level beyond the vacuum level.
- 2) Transport of the electrons to the surface of the material.
- 3) Emission of the electrons that reach the material surface and have enough kinetic energy to cross the surface potential.

The model that considers these three steps individually is called the three-step model.

On the other hand, from the point of view of quantum mechanics, a model that treats the three processes described above in a unified manner, known as the one-step model, is suggested. In the one-step model, the whole process from the initial states (the electronic states within the material) to the final state, which incorporates all scattering processes experienced by the photoelectron until it reaches the detector (represented as a time-reversed low-energy electron diffraction state), is considered simultaneously. Consequently, the one-step model reproduces the experimental PES results more accurately than the three-step model. Also, in recent years, some experimental results of PES have been reported that cannot be explained by the three-step model but can be accounted for by the one-step model [118, 119]. Nevertheless, because of the substantial cost of the one-step model calculation, the three-step model is commonly employed in practice.

2.2.1.1 Photoexcitation of electrons

Considering the process where an N -electron system is excited from an initial state (ground state) $|\phi_i^N\rangle$ to a final state (excited state) $|\phi_f^N\rangle$ by absorbing a photon with energy $h\nu$ or $\hbar\omega$. Assuming that the energy eigenvalue of the initial and final states are E_i^N and E_f^N , respectively, and the perturbation Hamiltonian describing the interaction between the photon and the electrons is $\mathcal{H}'$, according to Fermi's golden rule, the transition probability $P_{i \rightarrow f}$ from the initial state to the final state is given by

$$P_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle \phi_f^N | \mathcal{H}' | \phi_i^N \rangle|^2 \delta(E_f^N - E_i^N - \hbar\omega) \quad (2.16)$$

The Hamiltonian $\mathcal{H}$ of an electron with mass m and charge e in an electromagnetic field

is given by

$$\begin{aligned}\mathcal{H} &= \frac{1}{2m}(\mathbf{p} - \frac{e\mathbf{A}}{c})^2 + \frac{e}{c}\phi \\ &= \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{2mc^2}|\mathbf{A}|^2 + \frac{e}{c}\phi\end{aligned}\quad (2.17)$$

where c denotes the speed of light, $\mathbf{A}$ and ϕ are the vector potential and scalar potential of the electromagnetic field, respectively. By performing an appropriate gauge transformation, ϕ can be easily set to zero. Furthermore, since the probability of two-photon processes is small, the quadratic term in $\mathbf{A}$ representing the processes involving two photons can be neglected. Therefore, the Hamiltonian can be simplified as

$$\begin{aligned}\mathcal{H} &= \frac{\mathbf{p}^2}{2m} - \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) \\ &= \mathcal{H}_0 - \frac{e}{2mc}(\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})\end{aligned}\quad (2.18)$$

Consequently, the perturbation Hamiltonian $\mathcal{H}'$ can be expressed by

$$\mathcal{H}' = \frac{e}{2mc}(\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A}) \quad (2.19)$$

By substituting the commutation relation in to equation 2.19, one obtains

$$\mathcal{H}' = \frac{e}{2mc}(2\mathbf{A} \cdot \mathbf{p} + i\hbar(\nabla \cdot \mathbf{A})) \quad (2.20)$$

where the vector potential $\mathbf{A}$ can be written in the form of a plane wave as

$$\mathbf{A}(\mathbf{r}, t) = A_0 e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (2.21)$$

In PES, particularly when using vacuum-ultraviolet photons, since the wavelength of the radiation (in the order of 100 Å) is much larger than the lattice constant of the materials (around several Å), within the long-wavelength approximation, the spatial variation of $\mathbf{A}$ can be neglected. Under this approximation, $\nabla \cdot \mathbf{A} = 0$, and therefore the perturbation Hamiltonian $\mathcal{H}'$ becomes

$$\mathcal{H}' = \frac{e}{mc}(\mathbf{A} \cdot \mathbf{p}) \quad (2.22)$$

Consequently, the transition probability can now be written as

$$P_{i \rightarrow f} \propto |\langle \phi_f^N | \mathbf{A} \cdot \mathbf{p} | \phi_i^N \rangle|^2 \delta(E_f^N - E_i^N - \hbar\omega) \quad (2.23)$$

In a real multielectron system, each electron experiences not only the interaction from the external potential, but also the potential created by all other electrons. This results

in a complicated many-body problem that is almost impossible to solve analytically. For simplicity, the interactions between an electron and the other electrons can be approximated by an effective mean field. Consequently, the situation could be considered as a single electron moving in this mean-field potential. Using this single-electron approximation, the wave function of the N -electron system can be separated into the wave function of the photoelectron and that of the rest $(N - 1)$ -electron system as

$$\phi_i^N = \psi_i \phi_i^{N-1} \quad (2.24)$$

$$\phi_f^N = \psi_f \phi_f^{N-1} \quad (2.25)$$

Here, ψ_i and ψ_f are the one-electron wavefunctions of the electron before optical excitation and that of the photoelectron generated by optical excitation, respectively. Similarly, ϕ_i^{N-1} and ϕ_f^{N-1} denote the wave function for the remaining $(N - 1)$ -electron system before photo excitation and after, and that of the $(N - 1)$ -electron ionic system after the photoelectron has been removed.

Substituting these separated wavefunctions into the matrix element of the transition probability in equation 2.16 yields

$$\langle \phi_f^N | \mathcal{H}' | \phi_i^N \rangle = \langle \psi_f | \mathcal{H}' | \psi_i \rangle \langle \phi_f^{N-1} | \phi_i^{N-1} \rangle \quad (2.26)$$

When the electron correlation is weak, the photoemission process induced by optical excitation has only a minor influence on the remaining $(N - 1)$ -electron system, and thus the overlap $\langle \phi_f^{N-1} | \phi_i^{N-1} \rangle$ can be approximated to be around one. In this case, PES results accurately reflect the electronic density of states (DOS) and the material's band dispersion.

In contrast, in strongly correlated systems, the above-mentioned approximation breaks down, and the value of the overlap $\langle \phi_f^{N-1} | \phi_i^{N-1} \rangle$ becomes apparently smaller than unity.

This is clearer when using the one-particle Green's function. For the process in which a photon removes one electron from an N -electron system, the one-particle Green's function describing the temporal and spatial evolution of the system is given by

$$G(\mathbf{k}, \omega) = \sum_f | \langle \psi_f^{N-1} | c_k | \psi_i^N \rangle |^2 \left[\frac{\mathcal{P}}{\omega + E_f^{N+1} - E_i^N} - i\pi\delta(\omega + E_f^{N-1} - E_i^N) \right] \quad (2.27)$$

where $\mathcal{P}$ is the Cauchy principle value, and c_k denotes the annihilation operator for a Bloch electron. Using the one-particle Green's function, the photoemission spectral function $A(\mathbf{k}, \omega)$ can be expressed as

$$A(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im } G(\mathbf{k}, \omega) \quad (2.28)$$

When electron-electron interaction can be neglected, the single-particle approximation yields

$$G(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon_k^0 + i0^+} \quad (2.29)$$

and thus the corresponding spectral function can be expressed by

$$A(\mathbf{k}, \omega) = \delta(\omega - \epsilon_k^0) \quad (2.30)$$

Here, ϵ_k^0 is the energy of the one-electron Bloch state, or in other words, the binding energy of the electron. In this case, the spectral function takes the form of a delta function at the binding energy. Therefore, spectra acquired from PES can directly provide the density of states and the energy dispersion of the electrons in the material.

On the other hand, if electron correlation is present, the quasiparticle picture, in which the interacting electron acquires a finite lifetime and its energy deviates from that of the non-interacting electrons, must be considered. For this purpose, the complex self-energy $\Sigma(\mathbf{k}, \omega)$, which quantifies deviations from the single-particle approximation, is introduced. Consequently, the one-particle Green's function and the spectral function are given by

$$G(\mathbf{k}, \omega) = \frac{1}{\omega - \epsilon_k^0 - \Sigma(\mathbf{k}, \omega)} \quad (2.31)$$

$$A(\mathbf{k}, \omega) = \frac{1}{\pi} \frac{-\text{Im} \Sigma(\mathbf{k}, \omega)}{[\omega - \epsilon_k^0 - \text{Re} \Sigma(\mathbf{k}, \omega)]^2 + [\text{Im} \Sigma(\mathbf{k}, \omega)]^2} \quad (2.32)$$

In this case, the spectral function exhibits a quasiparticle peak with a width of $2\text{Im}\Sigma(\mathbf{k}, \omega)$, together with broad incoherent features on both sides of the peak, and the photoemission spectra no longer directly correspond to the DOS or the energy dispersion.

In addition, while only the electronic configuration with the lowest energy needs to be considered for the initial state (ground state), the final states do not correspond one-to-one with the initial state. Instead, it must be expressed as a linear combination of all possible electron configurations.

In photoexcitation, when an electron is excited and emitted, a hole is created in the corresponding shell. If the material contains unpaired electrons in the outer orbitals, especially in strongly localized $3d$, $4f$, or $5f$ shells, the exchange interaction and spin-orbit coupling between the hole induced by photoemission, thus generate multiple possible final states. Therefore, a complex structure with multiple peaks will appear in the PES spectra, which is known as the multiplet splitting [120, 121].

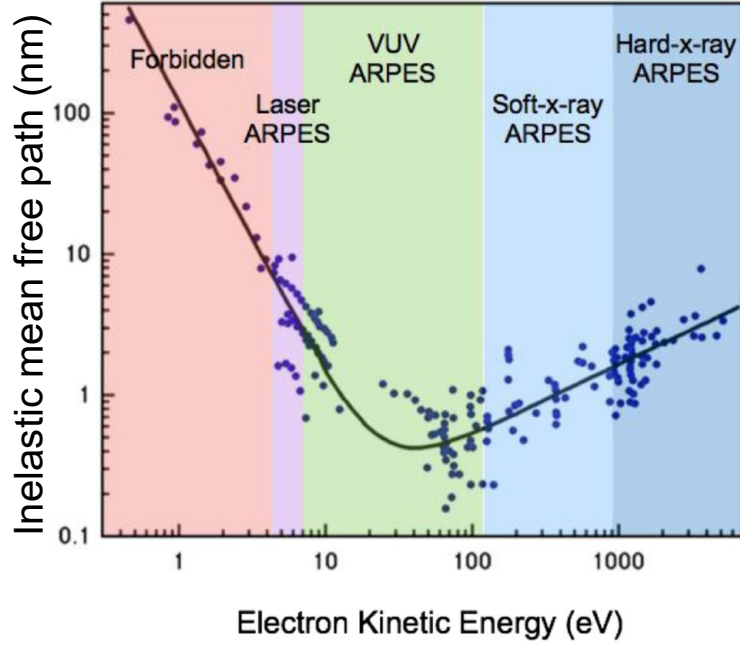


Figure 2.14: Universal curve of photoelectron inelastic mean free path as a function of the electron kinetic energy [122, 123].

2.2.1.2 Transport of the electrons to the surfaces of the material

In PES measurements, photons in the ultraviolet or x-ray region, with energies ranging from several eV to several keV, are commonly used. These photons can penetrate into the surface of the material for a range from several tens of nanometers up to a few micrometers. Consequently, the absorption of photons and thus the resulting excitation of electrons occur not only near the surface, but also deep within the bulk of the material.

However, the detection depth of PES measurements is rather determined by the escape depth of electrons. For an excited electron to escape from the sample and to be detected as a photoelectron, it must reach the sample surface without undergoing any inelastic scattering that would cause an energy loss. The electrons that are excited deeper inside the material thus have a lower probability of reaching the surface without undergoing energy decay.

The escape depth of an electron could be evaluated by the inelastic mean free path of the electron, i.e., the average distance that an electron can travel in the material without inelastic scattering. Although the inelastic mean free path depends on the material to some degree, the overall relationship between the inelastic mean free path and the kinetic energy of the electrons follows a common tendency that is known as the universal curve [122, 123], as shown in Fig. 2.14. According to the universal curve, for the electron with kinetic

energies of approximately 50-100 eV, typically in the PES measurement using photons in the vacuum-ultraviolet (VUV) region, the inelastic mean free path reaches the minimum to be about 0.3-0.5 nm, which is in the same order as the lattice parameter of most materials, making it a highly surface-sensitive measurement. Meanwhile, when using x-rays as the light source, electrons with kinetic energies of several hundred to several thousand eV exhibit an inelastic mean free path of several nanometers, making them more bulk-sensitive than PES using VUV light, but still surface-sensitive compared with many other measurements.

The characteristic shape of the universal curve primarily arises from electron-electron scattering accompanied by interband transitions, which constitute the dominant mechanism of electron energy loss as electrons propagate through the material. Since the occurrence of interband transition typically needs an energy of several eV, the scattering together with interband transitions is thus energetically forbidden for the low-energy electrons, resulting in a long inelastic mean free path. On the other hand, for electrons with high kinetic energies, the probability of interband excitation decreases, while the increased velocity allows electrons to travel longer distances before being scattered.

2.2.1.3 Emission of photoelectron

To escape from the material, an electron that reaches the surfaces must possess a kinetic energy component normal to the surface that exceeds the surface potential barrier, namely the work function Φ , as shown in Fig. 2.13. A model in which the final state of photoexcitation is approximated by a free-electron-like parabolic dispersion is schematically shown in Fig. 2.15. Here, E_0 , E_F , and E_{vac} denote the bottom of the band of the final state, the Fermi level, and the vacuum level, respectively. The energy difference between the vacuum level and the Fermi level corresponds to the work function Φ , and that between the vacuum level and the bottom of the final state band is referred to as the inner potential U_0 .

Only electrons that satisfy

$$\frac{\hbar^2}{2m} k_{\perp}^2 \geq E_{\text{vac}} - E_0 = U_0 \quad (2.33)$$

can escape from the sample surface into the vacuum. The kinetic energy of an electron after emission from the surface of the material is thus given by

$$E_{\text{kin}} = E_f - E_{\text{vac}} \quad (2.34)$$

where E_f is the final state energy after photo excitation.

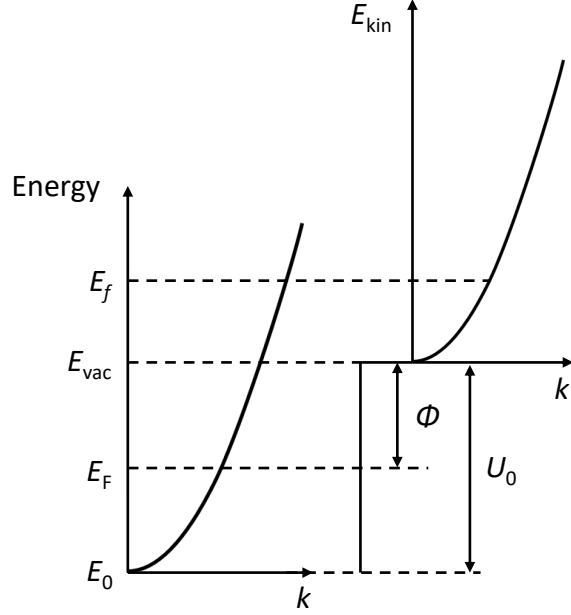


Figure 2.15: Schematic illustration of a model that treats the free-electron-like final state of photoexcitation

2.2.2 Angle-resolved Photoelectron Spectroscopy (ARPES) [120, 124]

Angle-resolved photoelectron spectroscopy (ARPES) is a variant of PES. In addition to measuring the kinetic-energy distribution of the photoelectron in the normal PES, ARPES also detects the angular distribution of the photoelectrons. This enables us to obtain information on both the kinetic energy (i.e., binding energy) and the emission angle (i.e., momentum) of the photoelectrons simultaneously, thereby allowing us to illustrate the electronic band structure of the material using ARPES.

The photoemission process of the electron from the material surface is schematically illustrated in Fig. 2.16. let us assume momentum of the electrons is $\mathbf{k} = (k_{\parallel}, k_{\perp})$ and $\mathbf{k}' = (k'_{\parallel}, k'_{\perp})$ when they are in the material and in the vacuum after being emitted from the sample surface, and define the emission angle of the photoelectron relative to the sample surface to be θ . Given an ideally flat surface, the in-plane component of the momentum of the electron should be conserved during the emission process, which gives

$$k_{\parallel} = k'_{\parallel} = k' \sin \theta \quad (2.35)$$

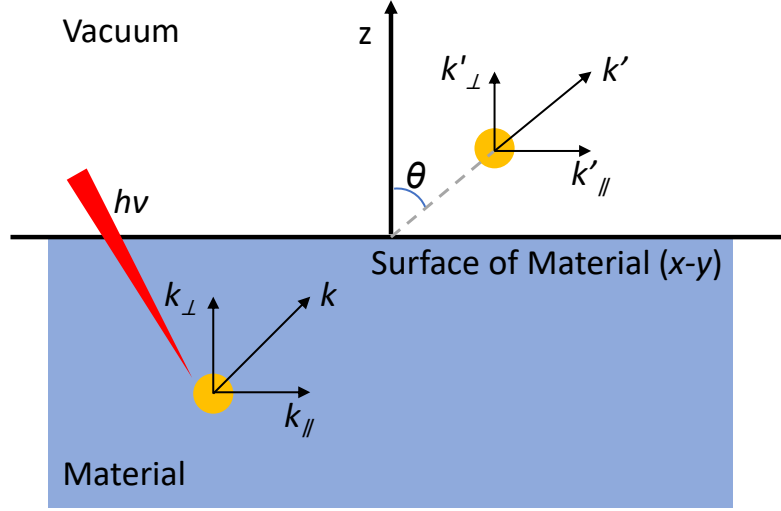


Figure 2.16: Schematic illustration of ARPES.

Furthermore, the kinetic energy of the emitted electron in the vacuum can be written as

$$E_{\text{kin}} = \frac{\hbar^2}{2m}(k_{\parallel}'^2 + k_{\perp}'^2) = \frac{\hbar^2}{2m}k'^2 \quad (2.36)$$

Combining equation 2.35 and 2.36, one can steadily acquire

$$\hbar k_{\parallel} = \sqrt{2mE_{\text{kin}}}\sin\theta \quad (2.37)$$

Using equation 2.15, we finally obtain

$$\hbar k_{\parallel} = \sqrt{2m(h\nu - \Phi - E_{\text{B}})}\sin\theta \quad (2.38)$$

From energy conservation along the direction perpendicular to the sample surface, we have

$$\frac{\hbar^2}{2m}k_{\perp}^2 = \frac{\hbar^2}{2m}k_{\perp}'^2 + U_0 \quad (2.39)$$

Rearranging this equation, one can easily get

$$\hbar k_{\perp} = \sqrt{2m(E_{\text{kin}}\cos^2\theta + U_0)} = \sqrt{2m((h\nu - \Phi - E_{\text{B}})\cos^2\theta + U_0)} \quad (2.40)$$

2.2.3 Dipole transition matrix element and polarization dependence in PES

In addition to the spectral function discussed in Section 2.2.1.3, the measured intensity in PES also depends on the dipole transition matrix element M_{fi} :

$$I(\mathbf{k}, \omega) \propto |M_{fi}|^2 A(\mathbf{k}, \omega) \quad (2.41)$$

$$M_{fi} = \langle \psi_f | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle \quad (2.42)$$

Here, A is the vector potential of the incident light, which is parallel to the electric field vector determined by the light polarization.

Usually, the polarization in a specific experimental geometry is defined as follows: The p -polarization indicates that the electric field lies within the scattering plane, while the s -polarization indicates that the electric field is perpendicular to the scattering plane. With respect to the scattering plane, the p -polarized light shows an even symmetry, while the s -polarized light shows an odd symmetry. When the scattering plane coincides with a mirror plane of the crystal, symmetry selection rules apply. Since the plane wave approximation can be applied to the final state (the photoelectron that is emitted into vacuum) in the PES measurement, ψ_f can be considered as even with respect to the mirror plane. Therefore, for p -polarized light, only the initial states that also even yield a nonzero matrix element. Conversely, for odd s -polarized light, the matrix element is finite only when the initial state is also odd. As a result, even initial states are selectively enhanced under p -polarization and odd initial states under s -polarization. This leads to complementary results from s - and p -polarized photons and enables selective probing of different orbital components via polarization-dependent measurements.

For example, assuming the scattering plane is the x - z plane, for p orbitals, p_x and p_z are even and thus clearly observed with p -polarized light, while the odd p_y can be selectively measured with s -polarized light. Samely, for d orbitals, even d_{z^2} , $d_{x^2-y^2}$ and d_{xz} are enhanced in measurement with p -polarized light, while d_{yz} and d_{xy} are suppressed.

2.2.4 k_z broadening

In ARPES measurement, photoelectrons can only be emitted from a finite depth λ below the sample surface, which is determined by the inelastic mean free path of the electrons,

dependent on the kinetic energy of the photoelectrons (and thus the photon energy), as shown in Fig. 2.14. This leads to an intrinsic uncertainty of out-of-plane momentum k_z of the photoelectron, known as k_z broadening. According to the uncertainty principle, the intrinsic uncertainty of k_z could be estimated by

$$\Delta k_z \approx \frac{1}{\lambda} \quad (2.43)$$

As a result, ARPES cannot probe a single well-defined k_z value but effectively averages over a finite range of k_z .

This effect is most apparent in ARPES measurement using vacuum-ultraviolet photons, where the escape depth λ of the photoelectrons is typically 3-5 Å, corresponding to $\Delta k_z \approx 0.2$ - 0.3 Å⁻¹, which is comparable to the Brillouin-zone size of the material with a large lattice parameter of about 20 Å. Meanwhile, at lower or higher photo energies (several eV in laser ARPES or several hundreds to several thousands eV in soft- or hard-x-ray ARPES), the influence of k_z broadening could usually be neglected because of the increasing escape depth of photoelectrons.

2.2.5 Core-level photoelectron spectroscopy [120]

In solids, electrons, except for the valence electrons, are bound to atoms in quantized energy levels with different binding energies. Commonly, x-ray photoelectron spectroscopy (XPS) is used to detect these states.

For s orbitals with zero orbital angular momentum, only a single peak is observed in XPS. In contrast, electrons in orbitals with nonzero orbital angular momentum (p , d , and f orbitals) exhibit spin-orbit splitting. This splitting originates from the interaction between the electron spin and its orbital angular momentum, resulting in two states with different total angular momentum given by

$$j = l + \frac{1}{2}, \quad j = l - \frac{1}{2}. \quad (2.44)$$

Consequently, two peaks appear in the XPS spectrum for these orbitals, while the intensity relation of these two peaks is determined by their degeneracies, which are proportional to $2j + 1$. For example, the intensity ratio of the $d_{5/2}$ and $d_{3/2}$ peaks is 3 : 2, while that of the $f_{7/2}$ and $f_{5/2}$ peaks is 4 : 3. Meanwhile, the magnitude of the spin-orbit splitting depends on the spatial extent of the orbital. In general, orbitals located closer to the nucleus exhibit larger splitting energies.

Even for the same element, the binding energy of a core-level electron depends on its chemical environment. When an atom forms chemical bonds, its local electronic structure changes, leading to shifts in the core-level peaks. This effect, known as the chemical shift, provides information about the chemical bonding state of the element.

Qualitatively, the shift in binding energy ΔE when an element changes from its elemental state A to a compound state B can be expressed as

$$\Delta E = K (q_A - q_B) + (V_A - V_B), \quad (2.45)$$

where q denotes the valence charge of the atom, K is a proportionality constant describing the interaction between valence and core electrons, and V is the Madelung potential given by $V = \sum \frac{q_j}{R_j}$, representing the summation of the electrostatic potential due to surrounding ions.

The first term reflects changes in the valence electron charge of the atom, while the second term represents the contribution from the surrounding electrostatic potential. In many cases, since the valence of the central atom and the surrounding atoms usually change oppositely, these two contributions act in opposite directions. Assuming the comparatively common case that the first term is dominant, when an atom becomes a cation, or in other words, is oxidized, its core levels shift to higher binding energies. In contrast, the core levels shift to lower binding energies when the atom becomes an anion.

2.3 X-ray diffraction (XRD)[125, 126]

X-ray diffraction is a powerful tool for characterizing thin-film samples, providing detailed information on the crystalline phase, lattice parameters, degree of crystallinity, film thickness, and other properties.

In this section, the general principles of XRD measurements and methods for characterizing thin-film samples will be introduced.

2.3.1 General principles of XRD

2.3.1.1 Lattice vector, reciprocal lattice vector and Miller index

For a crystal with a primitive lattice vectors of $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, an arbitrary lattice vector can be shown as

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (2.46)$$

where n_1 , n_2 , and n_3 are arbitrary integers. Meanwhile, the corresponding primitive vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ of the reciprocal lattice are defined as

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.47)$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.48)$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad (2.49)$$

and

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij} \quad (2.50)$$

An arbitrary reciprocal lattice vector can be written as

$$\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 \quad (2.51)$$

in which h , k , and l can be arbitrary integers.

Due to the translational symmetry in a crystal,

$$\exp(i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})) = \exp(i\mathbf{K} \cdot \mathbf{r}) \quad (2.52)$$

and thus

$$\exp(i\mathbf{K} \cdot \mathbf{R}) = 1 \quad (2.53)$$

$$\mathbf{K} \cdot \mathbf{R} = (n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) \cdot (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) = 2n\pi \quad (2.54)$$

Each set of h , k , and l defines a set of crystal planes that intersect the crystallographic axes at $(x, y, z) = (a_1/h', a_2/k', a_3/l')$, where (h, k, l) is the smallest integer ratio of (h', k', l') . The expression (hkl) is used to express the above-mentioned set of lattice planes, and is known as the Miller indices.

In general, the normal direction of the (hkl) plane and the $[hkl]$ direction are not parallel. The exceptions are the cubic crystals, where $\mathbf{a}_i \parallel \mathbf{b}_i$ and thus $[hkl]$ direction is perpendicular to (hkl) plane.

2.3.1.2 Bragg's Law

X-rays that incident on the material will be scattered by the electrons in the material. In a single crystal, a well-defined order of the atoms exists. Given that the wavelength of the x-ray, for example, 1.5418 Å for the Cu K α line, is in the same order of magnitude as that

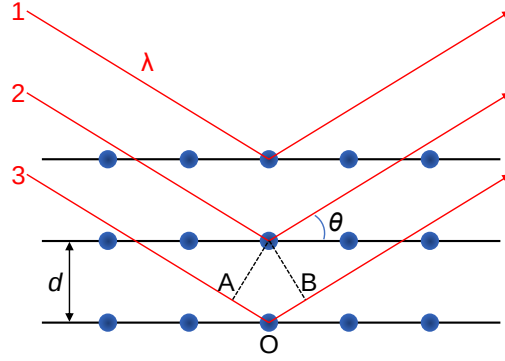


Figure 2.17: Schematic illustration of Bragg Condition

of the spacing of atoms in the crystals (several Å), constructive and destructive interference of the scattered electrons can be observed.

Figure 2.17 schematically illustrates the situation in which the x-ray incident into a series of ordered lattice planes. Considering the elastic scattering of the photons, and including the assumptions that treating the lattice plane as a mirror plane, the law of specular reflection could be used. Assuming that the angle between the incident x-ray and the lattice plane is θ , and the distance between two adjacent lattice planes is d , the path difference ΔL between x-rays scattered from neighboring planes is given by

$$\Delta L = AO + OB = 2d\sin\theta \quad (2.55)$$

Meanwhile, assuming the wavelength λ of the incident photons, the condition for constructive interference is given by

$$\Delta L = n\lambda \quad (2.56)$$

Consequently, we have

$$2d\sin\theta = n\lambda \quad (2.57)$$

Equation 2.57 is known as the Bragg equation, where n is an arbitrary integer. The Bragg equation establishes the relationship between the spacing of lattice planes d , the incident and diffracted angle, and the wavelength λ of the x-ray, which serves as the foundation of all XRD analysis.

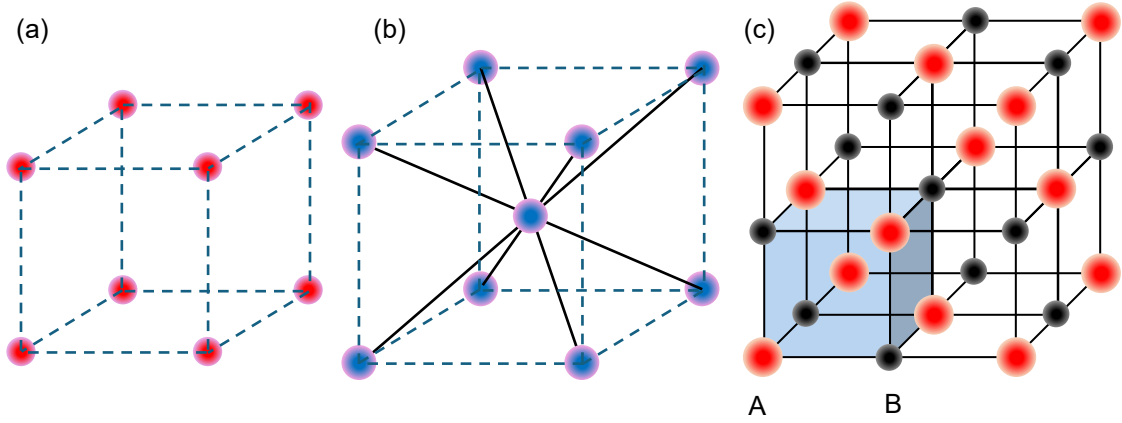


Figure 2.18: Schematic illustration of (a) simple cubic structure, (b) body-centered cubic structure, and (c) face-centered cubic structure.

2.3.1.3 Extinction rules [127, 128]

In the x-ray diffraction measurements, sometimes Bragg peaks of certain Miller indices are absent. This absence arises from the symmetry of the crystal lattice, the type of atoms contained, and the arrangement of atoms in the unit cell, which leads to destructive interference of the scattered x-ray. The condition where this absence occurs is described by the extinction rules.

In general, the intensity of the reflected x-ray from a lattice plane with Miller indices of (hkl) is given by

$$I(hkl) \propto |F(hkl)|^2 \quad (2.58)$$

$$F(hkl) = \sum_j^n f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (2.59)$$

where $F(hkl)$ is known as the structure factor, f_j is the atomic scattering factor of atom j , n is the number of atoms in a unit cell, and x_j, y_j, z_j are the coordinates of the atom j in the unit cell.

From Equation. 2.58 and 2.59, one can find out that the condition makes $F(hkl) = 0$, the corresponding Bragg peaks disappear, or in other words, the distinction of the Bragg peaks happens.

Here, we use the primitive cubic structure, body-centered cubic (bcc) structure, and face-centered cubic (fcc) rock salt structure as examples to illustrate how the extinction rules work.

For the simple cubic structure, as shown in Fig.2.18 (a), there is only one atom at (0, 0, 0) in the primitive cell. Consequently, its structure factor could be written as

$$F(hkl) = fe^{2\pi i(0)} = f \quad (2.60)$$

Therefore, unless $f = 0$, which is not physically possible, $F(hkl) \neq 0$ has a finite value. As a result, reflection from the crystal plane with all Miller indices (hkl) is allowed by the extinction rules, and thus could be observed in XPS measurement.

For the bcc structure, as shown in Fig. 2.18 (b), the situation is slightly complex compared to the simple cubic structure. In the primitive cell, two identical atoms are located at (0, 0, 0) and (1/2, 1/2, 1/2). Inputting these values into equation 2.59, we get

$$F_{bcc}(hkl) = f(1 + \exp(\pi i(h + k + l))) \quad (2.61)$$

Therefore, there are two kinds of conditions as follows: When $(h + k + l)$ is even, $F_{bcc}(hkl) = 2f$, and the diffraction is thus permitted. On the other hand, when $(h + k + l)$ is odd, $F(hkl)$ becomes zero. This means that any reflection from the lattice plane whose Miller indices sum to an odd number would be completely absent in the XRD measurement.

The fcc rock salt structure is shown in Fig. 2.18 (c). There are two different kinds of atoms in the primitive unit cell marked by the grey area: atom A locates at (0, 0, 0), (0, 1/2, 1/2), (1/2, 0, 1/2), (1/2, 1/2, 0), and atom B locates at (1/2, 1/2, 1/2), (1/2, 0, 0), (0, 1/2, 0), (0, 0, 1/2). Using equation 2.59, the structure factor $F(hkl)$ can be separated into three different situations. When h , k , and l are all even numbers, the structure factor given by

$$F_{even}(hkl) = 4(f_A + f_B) \quad (2.62)$$

reaches the maximum, and the intensity of the diffraction is considered to be high. On the other hand, when h , k , and l are all odd number, we have

$$F_{odd}(hkl) = 4(f_A - f_B) \quad (2.63)$$

In this case, the diffraction factor is in general not zero, but proportional to the difference between f_A and f_B . For the last case, if both odd numbers and even numbers show in the (hkl),

$$F_{mixed}(hkl) = 0 \quad (2.64)$$

and the reflection from the labelled lattice planes will be absent in the XRD results.

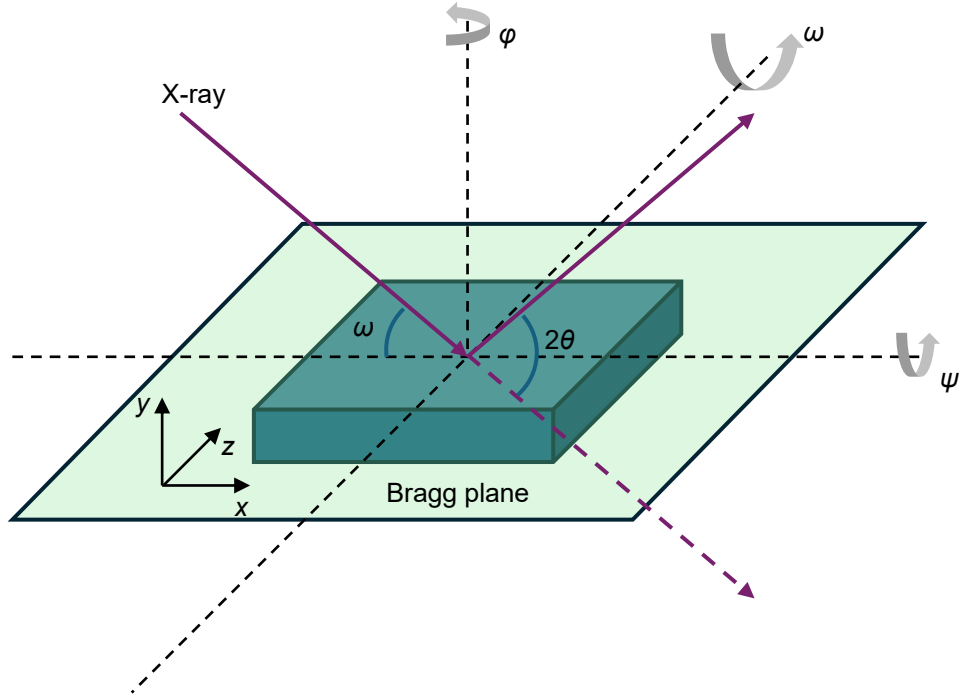


Figure 2.19: Schematical illustration of the typical geometry for the XRD measurement of thin films

2.3.2 General methods

Figure 2.19 exhibits the general setup of the XRD measurement for the thin film samples. There are seven different parameters, in which x , y , and z are primarily used to align the sample, while other parameters ω , θ , ϕ and ψ (or $\chi = 90^\circ - \psi$) are not only needed for alignment but can also form different kinds of measurements in XRD through their combinations. In this study, the ω - 2θ scan, rocking curve (ω scan), in-plane ϕ scan, and x-ray reflectivity (XRR).

In this subsection, the four measuring methods mentioned above will be briefly introduced.

2.3.2.1 ω - 2θ scan

The ω - 2θ scan is the most fundamental XRD measurement, where the ω and θ are varied following the restriction that ω is always the same value as θ , while the other parameters are kept unchanged. Therefore, the diffraction plane remains parallel to a specific surface (usually the sample surface), and only crystal planes oriented in a particular plane can thus

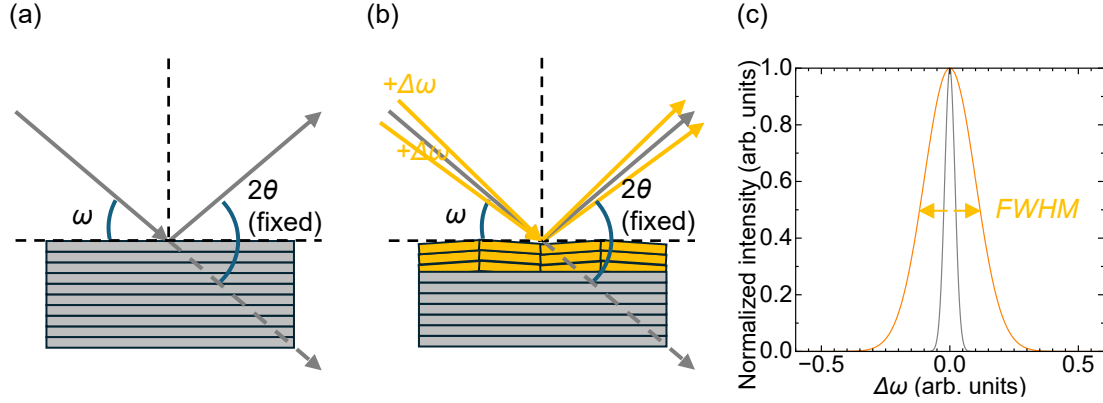


Figure 2.20: Schematic illustration of rocking curve measurements: (a) on an ideal surface of a single-crystal sample and (b) on the surface of a "real" film with grains whose lattice planes are slightly misaligned. An example of the measured rocking curve for these two situations is shown in (c).

satisfy the Bragg condition and be detected.

As a result, from the data of the ω - 2θ , the out-of-plane orientation of the thin film sample could be determined by the Miller indices of the observed peak. Meanwhile, using the Bragg equation, the periodicity of the detected series of lattice planes, and thus the out-of-plane lattice parameter, could be derived.

Information on the growth mode of the thin film samples is also included in the result of the ω - 2θ scan.

In epitaxial films, only the reflections from a single family of lattice planes should be observed. Meanwhile, one should note that the $\omega - 2\theta$ scan alone cannot confirm the in-plane alignment, but rather a combination with other measurements is required.

On the other hand, in textured or polycrystalline films, additional reflections from other families of lattice planes will also appear in the $\omega - 2\theta$ scan. In the extreme case of a completely randomly oriented polycrystalline film, the results would resemble powder XRD patterns, with some low-intensity reflections possibly missing due to the limited thickness of the thin-film sample.

2.3.2.2 Rocking curve (ω scan)

A rocking curve is obtained by fixing the angle of the detector (2θ) to the Bragg angle of a chosen reflection, and then scanning ω to tilt (or "rock") the sample. Tilting moves planes

that are slightly misaligned with respect to the surface into the Bragg condition. Therefore, the result of the ω scan is typically a single peak, whose width reflects how uniformly the lattice planes are aligned.

The full width at half maximum of the rocking curve is commonly used to evaluate the structural quality of the thin films. As shown in Fig. 2.20, in an ideal single-crystal thin film sample with a completely flat surface, the rocking curve is expected to be a single peak with a narrow width, which is determined by the instrument resolution. In contrast, in a real epitaxial thin-film system, because of the existence of the mosaic spread of the grains, density of dislocations, and substrate curvature, which would disrupt the parallel nature of the lattice planes, resulting in a broader curve in the rocking curve compared to the ideal case. Therefore, the smaller the FWHM of the rocking curve, the better the structural quality of the thin film is indicated to be.

2.3.2.3 In-plane ϕ scan

As introduced previously, the information of the in-plane crystallographic orientation of a thin film cannot be obtained from ω - 2θ scans or rocking curves alone. ϕ scan is a complementary method for this purpose.

In a ϕ scan, ω and 2θ are set to the Bragg condition of the reflection from a selected lattice plane that is not parallel to the sample surface. Then, the sample surface is tilted by choosing the appropriate ψ angle to align the selected lattice plane to the Bragg plane. For example, a (100)-oriented cubic film needs a ψ value of 54.7° for the (111) or (222) reflections, while its (011) or (022) peaks will appear at $\psi = 45^\circ$. Finally, the azimuth of the sample will be scanned through $\phi = 0-360^\circ$. When the grains with the corrected in-plane alignment satisfy the Bragg condition, the reflection peaks will appear.

From the ϕ scan, the number and the symmetry of peaks reveal the in-plane orientation of the films and also their relationship with that of the substrate. For example, a (100)-oriented cubic film with a single in-plane variant exhibits several series of four peaks with an even spacing of 90° , such as the (011), (0 $\bar{1}$ 1), (0 $\bar{1}\bar{1}$), (01 $\bar{1}$) family, and the (111), (1 $\bar{1}$ 1), (1 $\bar{1}\bar{1}$), (11 $\bar{1}$) family at above-mentioned ψ value. Similarly, for the (111)-oriented cubic film, the peaks would show a 6-fold symmetry. In contrast, if multiple orientations or rotational variants exist, additional peaks or peaks with different symmetry would emerge.

Meanwhile, assuming that the substrate is also crystallized in a cubic structure with (100) orientation, the relationship of the position of the same series of reflections between the film and the substrate directly reflects the in-plane rotation of the film with respect to the substrate.

By combining the ϕ scan with the scanning ψ , a two-dimensional map with several series of reflection peaks mentioned above could be obtained, which is known as a pole figure. Compared to the ϕ scan, the pole figure would give a more systematic and instinctive view of the in-plane crystallographic orientation of the thin-film sample. However, it also takes much longer to acquire the data and is thus usually only adopted when necessary.

2.3.2.4 X-ray reflectivity (XRR) [129, 130]

X-ray reflectivity (XRR) is an effective method for determining the properties of thin-film samples, including thickness, density, and surface or interface roughness.

To be accurate, the XRR measurement is not a part of XRD, since it does not rely on the diffraction phenomenon. However, it shares a similar measuring method to the ω - 2θ scan, and the only difference is that the value of ω and 2θ is much smaller for the grazing incidence, and the interference of the x-rays reflected by the surface and interfaces, rather than that reflected by the lattice plane, is observed.

Because the refractive index of materials of x-rays is slightly less than 1, the critical angle of the total reflection for x-rays incident into the sample surface is expected to be a small value of θ_c . This divides XRR into three different parts that, when scanning ω (which is equivalent to θ here in XRR) from 0 to several degrees.

Figure 2.21 exhibits the different situations dependent on the relationship between θ and θ_c in the XRR measurements.

When $\theta < \theta_c$, as shown in Fig. 2.21 (a), total reflection of x-ray happens on the surface of the sample, and a uniform intensity of the reflected x-ray is expected (usually applicable for real systems because of the imperfection of the surface).

Under the condition that the grazing angle is exactly equal to the total reflection critical angle, as shown in Fig. 2.21 (b), part of the incident x-rays propagates along the sample surface, and the intensity of the reflected x-ray starts to drop.

In the last case, where $\theta > \theta_c$, incident x-rays could penetrate into the sample by refraction, as shown in Fig. 2.21 (c). In this region, the reflectivity decreases rapidly with

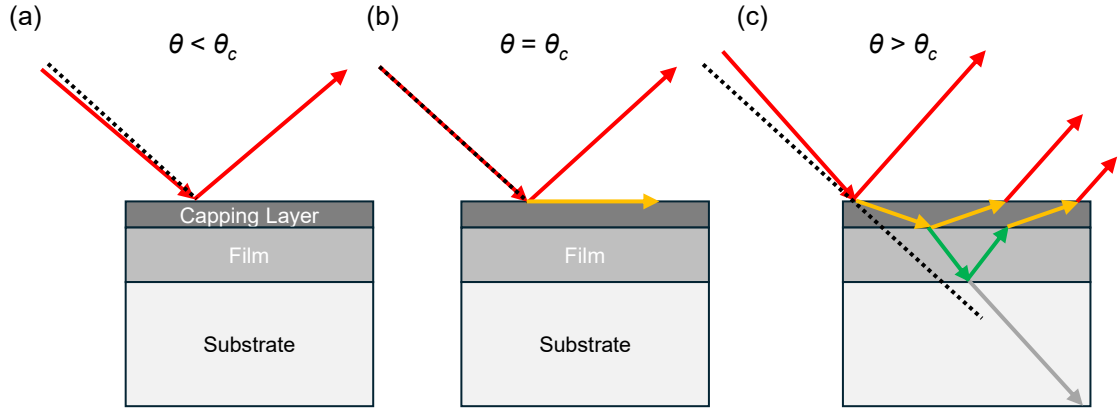


Figure 2.21: Schematic illustrations of the three different conditions in the XRR measurement depending on the relationship between the total reflection critical angle and the grazing angle of x-rays. The angles and layer thicknesses are exaggerated for clarity.

increasing θ , and falls roughly with θ^{-4} . Meanwhile, x-rays penetrating the sample surfaces are further reflected or refracted at the interfaces, leading to interference between the x-rays reflected by the sample surfaces and those reflected by the interfaces of the thin-film system.

Figure 2.22 exhibits a typical curve of a multilayered thin-film system measured by the XRR measurement. As indicated in the figure, several structural parameters of thin film, such as thickness, density, and surface/interfaces roughness, can be extracted from the shape of the XRR curve.

As briefly mentioned above with Fig. 2.21 (c), when $\theta > \theta_c$, x-rays penetrate the sample surfaces, and the interference of the reflections from both the film surface and the interface(s) could be observed while scanning θ . For a single-layered film, the Film thickness d can be easily calculated from

$$d = \frac{\lambda}{2\Delta\theta \cos \theta} \quad (2.65)$$

where λ is the wavelength of the incident x-ray, $\Delta\theta$ is the distenced between the nabouring fringes.

Given that θ is very small in the XRR measurements because of the grazing incidence, and using the small-angle approximation, equation 2.65 could be further simplified to be

$$d = \frac{\lambda}{2\Delta\theta} \quad (2.66)$$

which is commonly used in most XRR measurements.

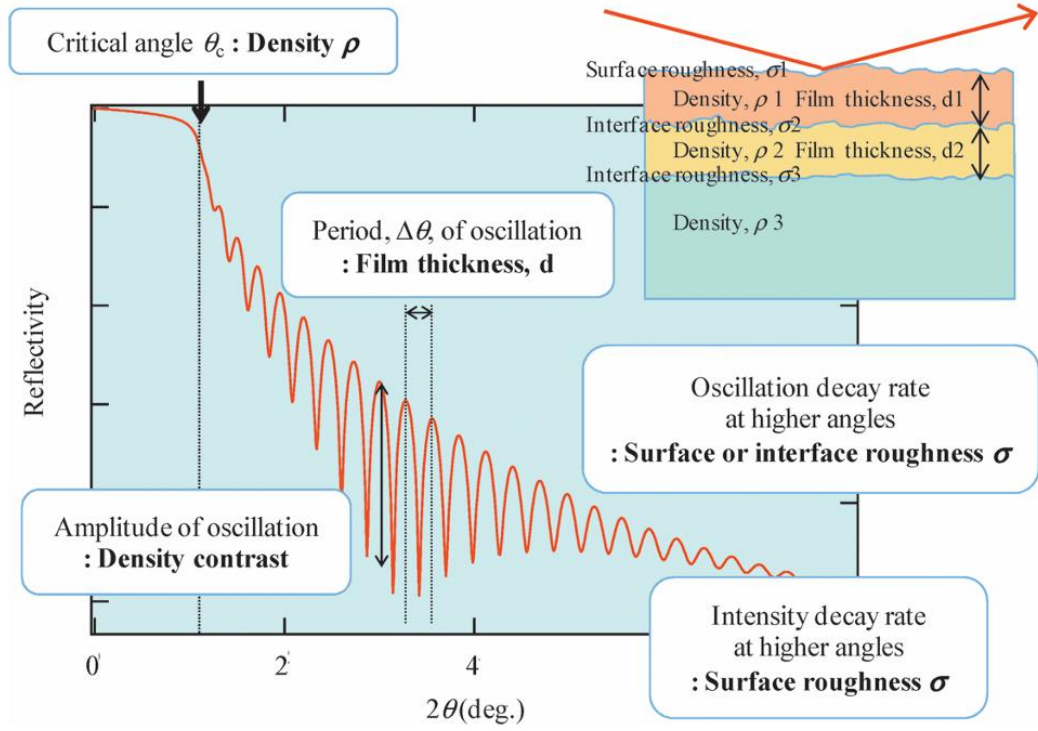


Figure 2.22: An example of the XRR results together with the information that could be extracted from the XRR profile [130].

For samples with more than one layer, oscillation with different periods would appear, and a fitting is usually needed to extract the thickness of each layer.

From the total reflection critical angle θ_c , which could be determined from the value at which the intensity of the reflected x-rays starts to drop quickly, the density of the top-most layer is given by

$$\rho = \frac{\theta_c^2 \pi M}{r_e \lambda^2 N_A Z} \quad (2.67)$$

in which θ_c is the total reflection critical angle in radians, M is the molar mass, r_e is the electron radius, λ is the wavelength of the incident x-ray, N_A is Avogadro's number, and Z is the total number of electrons per formula unit (atomic number for elementary materials).

Besides the film thickness and the density of the topmost layer, the density contrast between layers and the surface/interface roughness can be extracted from the oscillation amplitude and the oscillation/intensity decay. In general, a larger oscillation amplitude indicates a greater density difference, and a slower decay rate suggests a flatter surface or

an intersurface. However, extracting the exact values of the surface/intersurface roughness and the densities of the embedded layers requires a much more complicated fitting of the entire XRR curve; thus, a detailed introduction is omitted here.

Chapter 3

Epitaxial YbN(100) thin films grown by nitrogen plasma-assisted MBE

In this chapter, we report the successful fabrication of epitaxial and stoichiometric ytterbium nitride (YbN) thin films on both MgO(100) and LaAlO₃(100) substrates. The well-defined (100) orientation and epitaxial growth were determined by *in situ* reflection high-energy electron diffraction (RHEED) together with *ex situ* x-ray diffraction (XRD). Furthermore, *in situ* photoelectron spectroscopy (PES) results demonstrate the semiconducting nature of YbN, the fully trivalent state of Yb ions, and a significant hybridization of Yb 4*f* and N 2*p* states.

3.1 Experimental Conditions

In this section, we introduce the experimental conditions for the growth study and the characterization of the YbN thin films.

3.1.1 Substrates

YbN thin films were grown by molecular beam epitaxy (MBE) on epi-polished MgO(100), LaAlO₃(100), and YVO₄(100) substrates. The MgO(100) substrates were purchased from Crystec GmbH, and the LaAlO₃ substrates were purchased from Crystall GmbH. MgO crystallizes in the face-centered cubic (fcc) rock salt structure with a lattice parameter of

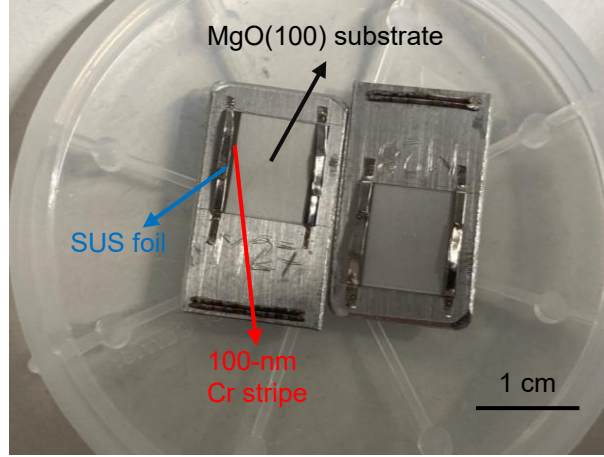


Figure 3.1: MgO(100) substrates mounted on the sample holders. 100-nm-thick Cr stripes were previously deposited near both the right and left edges of the substrate. The SUS stripes with a ring-like structure were used to fix the substrates onto the sample holder. The ring with springiness suppresses the Cr stripes firmly, ensuring fair electric contact between the sample surface and the substrate, and thus preventing the charging effect during PES measurements when a metallic or semiconducting film is grown on the surface.

4.21 Å. Considering the reported bulk lattice parameter 4.7852 Å of YbN [68], the lattice mismatch between MgO(100) and YbN(100) is about -13.7 %. LaAlO₃ is cubic perovskite structured with a lattice parameter of 3.79 Å. Although the lattice mismatch between LaAlO₃(100) and YbN(100) is as large as -26.3 %, a lattice parameter of 5.36 Å and a moderate lattice mismatch of about +10.7 % could be applied when YbN films with out-of-plane (100) orientation grow on LaAlO₃(100) surface with a 45 ° in-plane rotation, i.e. [010] direction of YbN(100) aligns with [011] direction of LaAlO₃(100). For YVO₄ crystallized in the tetragonal Zircon structure with a lattice parameter of 7.12 Å for the (100) plane. Similar to the case of LaAlO₃, despite the large lattice mismatch, an effective lattice parameter of 5.04 Å and a lattice mismatch of +5 % could be applied when a 45 ° in-plane rotated growth is considered.

Before being loaded into the ultra-high vacuum (UHV) system, the substrates were cleaned in acetone and isopropanol using an ultrasonic bath. Due to the insulating nature of the substrates, approximately 100 nm-thick Cr stripes were subsequently deposited in a separate chamber near both left and right edges. This ensured moderate electrical conduction between the sample surface and the sample holder, thereby preventing charging during the PES measurement. A photo of the prepared substrates mounted on the sample

holders is shown in Fig. 3.1. The substrates were then annealed in an O_2 atmosphere ($P_{\text{O}_2} = 1 \times 10^{-6}$ mbar) at 600 °C for 2 hours to produce a well-ordered surface for epitaxial growth.

3.1.2 MBE system

The MBE growth of YbN thin films was conducted using the MBE system equipped with a radio-frequency (RF) plasma source and five standard Knudsen effusion cells (Luxel Corporation) at the MBE lab, Department of Physics of Correlated Matter, Max Planck Institute for Chemical Physics of Solids (MPI CPfS) in Dresden, Germany. The base pressure of the MBE system was maintained to be approximately 1×10^{-10} mbar.

High-purity Yb metal, which is additionally refined in a Ta ampule, was evaporated from one of the effusion cells. A quartz crystal thickness monitor at the deposition position was used to measure the Yb effusion cell flux rate before and after each growth. For growth optimization, the Yb flux rate (ϕ_{Yb}) was varied from 1 Å/min to 10 Å/min, corresponding to the temperature of the Yb effusion cell varying from 335 °C to 410 °C. By thoroughly degassing the Yb effusion cell, the MBE system pressure was maintained below 5×10^{-9} mbar even at the highest Yb flux rate of 10 Å/min, ensuring a super-clean environment for epitaxial growth.

Unless otherwise specified, the growth time was adjusted to maintain a fixed total Yb deposition of 240 nm.

Nitrogen was supplied via an RF plasma source (UNI-Bulb RF Plasma Source for Veeco). High-purity nitrogen was introduced to the MBE system via the RF plasma source, without igniting the nitrogen plasma, for molecular nitrogen supply. Nitrogen flow was set to 0.43 SCCM (standard cubic centimeter per minute) for a nitrogen pressure of P_{N_2} . For the supply of activated nitrogen, the power of the plasma source was varied from 100 to 200 W, while the nitrogen flow was adjusted from 0.1 to 0.4 SCCM for the growth optimization. During growth, the pressure in the growth chamber was 2.5×10^{-6} mbar at 100 W/0.1 SCCM, and increased to 1×10^{-5} mbar at 200 W/0.4 SCCM. The distance between the plasma source and the sample surface was set to 10 cm.

The substrate was heated by thermal radiation from a filament during the growth. Different substrate temperatures (T_{sub}), ranging from room temperature (about 30 °C) to 400 °C, were chosen for each film to optimize the growth conditions.

3.1.3 Characterization of YbN thin films

During the deposition process, an *in situ* RHEED system (STAIB Instrument RH35, acceleration voltage = 20 kV) was employed to characterize the surface atomic structure of the substrates and the fabricated thin films. The electronic structure, chemical composition, and Yb valence state were subsequently investigated by *in situ* x-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS). During synthesis, sample transfer, and PES measurement, the films were maintained in a UHV environment at a background pressure of about 1×10^{-10} mbar. For XPS measurement, Monochromated Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) was used, and the energy resolution was estimated to be approximately 0.4 eV by measuring the Fermi edge of the Ag reference sample. UPS measurements were taken using He-I radiation ($h\nu = 21.2$ eV) from a helium discharge lamp without monochromation. The energy resolution of UPS measurements was estimated to be approximately 0.1 eV.

The detailed crystalline structure of the fabricated films was further analyzed using *ex situ* XRD. To prevent sample degradation in air, approximately 10-nm-thick Cr capping layers were deposited on the sample surface. XRD measurements were conducted using a PANalytical X'Pert PRO diffractometer with monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.54056\text{\AA}$).

3.2 Attempt to grow YbN thin films with molecular nitrogen

As introduced in previous chapters, unlike many other rare-earth (*RE*) elements, Yb is reported to be incapable of catalyzing the dissociation of nitrogen molecules, and thus YbN layers could not be formed by depositing Yb atoms onto a substrate in a N_2 atmosphere [27]. To confirm this, we first attempted to grow YbN on a MgO substrate using molecular nitrogen. A high nitrogen pressure of 1×10^{-5} mbar, which is the optimal value for the growth of SmN and HoN with molecular nitrogen. The substrate temperature (T_{sub}), Yb flux rate (ϕ_{Yb}), and growth time were set to be room temperature, $2.5 \text{ \AA}/\text{min}$, and 120 min.

Figure 3.2 shows the RHEED pattern of the MgO substrate acquired just before the growth, together with the RHEED pattern measured just after the growth under the above-

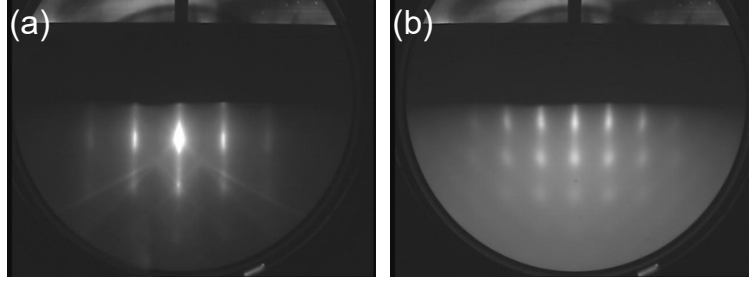


Figure 3.2: RHEED patterns of the MgO(100) substrate acquired just before the growth (a), and that of the film measured just after the growth by directly depositing Yb atoms onto the MgO(100) substrates in an N_2 atmosphere.

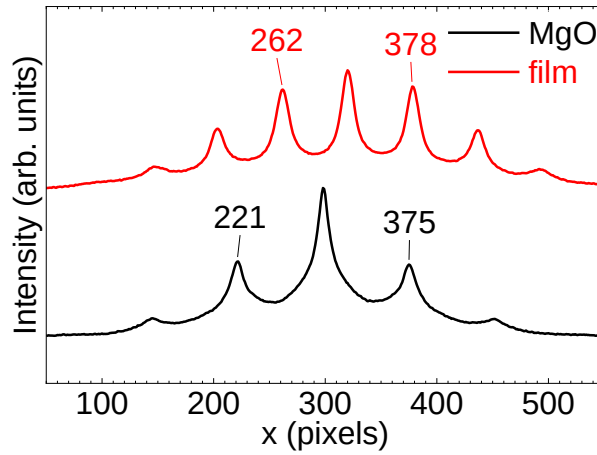


Figure 3.3: RHEED line profile of (a) MgO(100) substrate, and (b) synthesized film extracted from 3.2. The peak positions used for calculating the lattice parameter were marked.

mentioned conditions. Surprisingly, even though the growth was conducted at room temperature, where no ordered growth is expected, transmission spots together with faint streaks were observed in the RHEED pattern, as shown in Fig. 3.2 (b). This suggests a surface between three-dimensional islands and an epitaxial surface with multiple steps.

By comparing the spacing of the RHEED streaks of MgO(100) substrate extracted with that of the fabricated thin-film sample, extracted from the line profile or RHEED pattern (Fig. 3.3), the lattice parameter of the film was determined to be $5.59 \pm 0.06 \text{ \AA}$, which is far from the reported bulk lattice parameter of YbN but closer to that of fcc-structured Yb metal ($5.48 \text{ \AA}$ [131]).

The chemical composition of the synthesized film was further analyzed by *in situ* XPS. Figure 3.4 (a) shows the XPS wide-range spectrum, in which the peaks attributed to Yb core levels, together with minor peaks attributed to O $1s$ core level and O KLL Auger

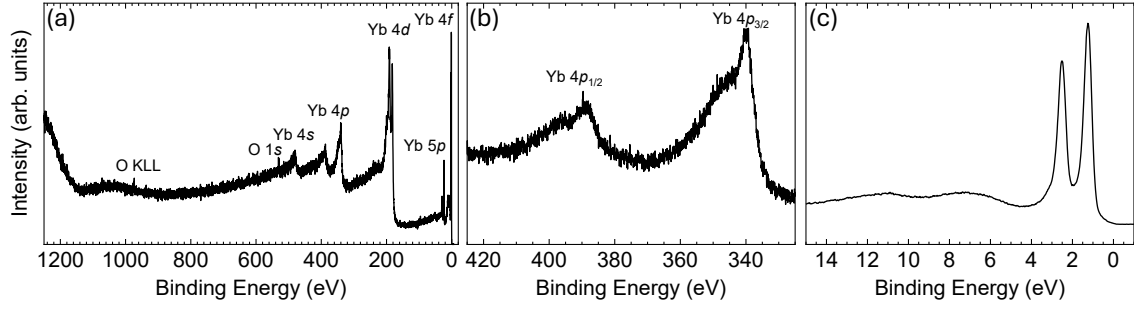


Figure 3.4: XPS spectra of the Yb-metal thin film grown on MgO(100) with molecular nitrogen at a nitrogen pressure of 1×10^{-5} mbar. (a) Wide range spectrum. (b) Yb 4p spectrum. (c) Valence band spectrum.

emission, could be observed. Meanwhile, no clear signal from nitrogen could be detected. The XPS spectrum zoomed in the binding energy region of 425-325 eV is shown in Fig. 3.4 (b). the features appear around 390 eV and 340 eV can be attributed to the $4p_{1/2}$ and $4p_{3/2}$ of Yb^{2+} , while the features of Yb^{3+} together with the sharp N 1s peak expected to appear at around 396 eV in *REN* [40, 43] are missing. In the valence band spectrum shown in Fig. 3.4 (c), sharp Yb $4f^{13}$ doublets at around 1.2 eV and 2.4 eV are observed, together with a very broad structure above 5 eV, where the Yb $4f^{12}$ multiplets are expected to appear in YbN thin films with mainly trivalent Yb composition. This valence band spectrum is well consistent with that of Yb metal, in which the Yb ions are predominantly divalent [132–134].

From the RHEED and XPS results above, we can conclude that the synthesized film is Yb metal rather than YbN. This finding supports the report on Yb’s inability to catalytically split nitrogen molecules [27], and thus the impossibility of growing YbN thin films with molecular nitrogen supply.

3.3 Optimization of growth conditions with RF plasma source

Since the growth of YbN thin films with molecular nitrogen supply was confirmed to be unfeasible, as discussed in the previous section, we introduce an RF plasma source to supply active nitrogen. In this section, we investigate the optimal conditions for the plasma-assisted MBE synthesis of YbN thin films.

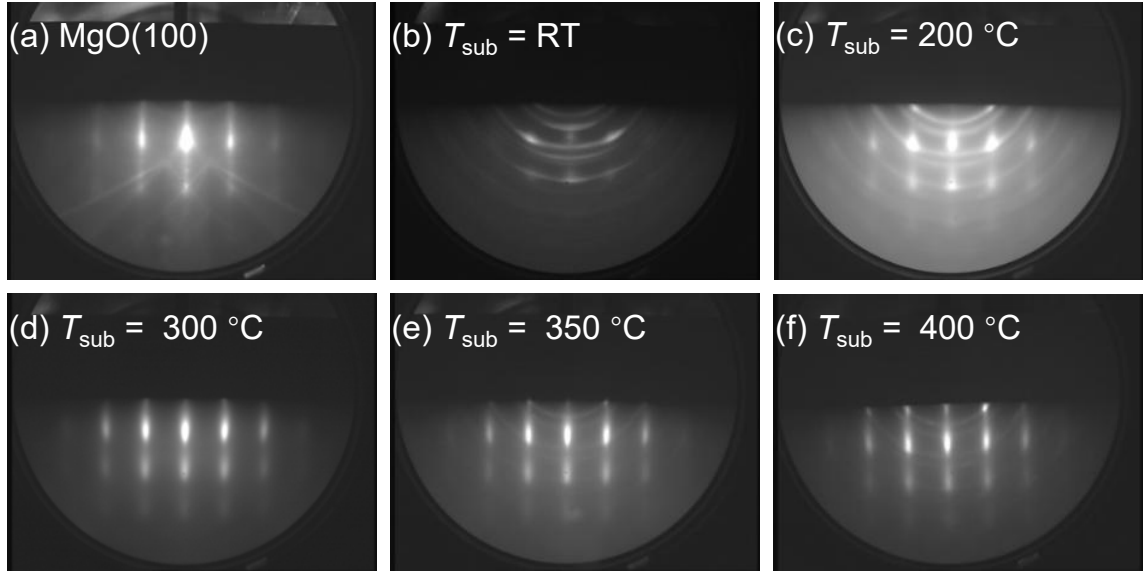


Figure 3.5: *In situ* RHEED images of (a) the MgO(100) substrate cleaned by annealing in O_2 atmosphere and of (b-f) YbN films grown at Yb flux rate of $5\text{ \AA}/\text{min}$, RF plasma-source power of 100 W , nitrogen flow of 0.1 SCCM , and indicated substrate temperatures. The incident electron beam was aligned parallel to the $[001]$ crystallographic direction of the MgO(100) substrate.

3.3.1 Optimization of the growth conditions on MgO(100)

3.3.1.1 Optimization of substrate temperature

We began by determining the optimal substrate temperature for epitaxial YbN growth on MgO(100) substrates. Figure 3.5 shows the RHEED patterns of a MgO(100) substrate and a series of thin films grown at different substrate temperatures ranging from room temperature (approximately $30\text{ }^{\circ}\text{C}$) to $400\text{ }^{\circ}\text{C}$. The power of the RF plasma source, nitrogen flow, and Yb flux rate were fixed at 100 W , 0.1 SCCM , and $5\text{ \AA}/\text{min}$, respectively. The film grown at room temperature exhibits a RHEED pattern with ring-like features and faint transmission spots, as shown in Fig. 3.5 (b), suggesting that the thin-film sample is primarily polycrystalline with some three-dimensional growth components. At a higher substrate temperature of $200\text{ }^{\circ}\text{C}$, as shown in Fig. 3.5 (c), the rings remain visible in the RHEED pattern, while the intensity of the transmission spots increases, becoming comparable to that of the ring-like features. This indicates improved crystalline quality with enhanced three-dimensional island growth and reduced polycrystallinity. At even higher substrate temperature, i.e., when $T_{\text{sub}} > 300\text{ }^{\circ}\text{C}$, as shown in Fig. 3.5 (d-f), synthesized thin films exhibit intensity modulated streaks in RHEED patterns, and become crisper with increasing substrate temperature. This suggests an epitaxial layer growth with several surface steps. Meanwhile, we also

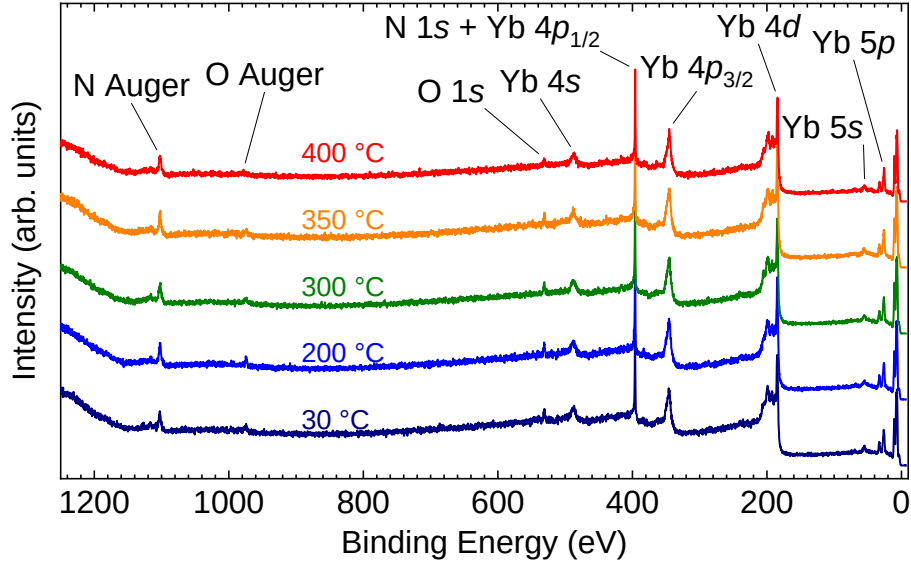


Figure 3.6: Substrate-temperature dependence of the XPS wide range spectrum of the YbN thin films grown on MgO(100) substrates at the RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, and Yb flux rate of 5 Å/min. Each spectrum is shifted upward for clarity.

noticed that in some of the epitaxial films grown at $T_{\text{sub}} > 300$ °C, faint ring-like structures could also be detected. This may be related to a minor disorder on the surface of the sample, as no significant effect on the XRD and XPS measurement results was observed.

By comparing the spacing of the RHEED streaks of the films with that of MgO(100) (Fig. 3.5 (a)), the lattice parameter was estimated to be 4.73 ± 0.06 Å, which is in agreement with the reported bulk lattice parameter of YbN of 4.7852 Å [68], within the measurement accuracy.

The composition and electronic structure of the fabricated thin-film samples were subsequently investigated using XPS. Figure 3.6 shows the wide-range XPS spectra of the same series of samples grown at different substrate temperatures, as those whose RHEED patterns are shown in Fig. 3.5 (b-f). Overall, the wide range XPS spectra of all the films are comparable. This suggests that although the films were grown at such different substrate temperatures varying from room temperature to as high as 400 °C and exhibited completely different crystalline quality, the chemical composition of the films remains similar. In the wide range spectra, peaks corresponding to the Yb 4s, 4p, 4d, 5s, and 5p core levels, together with the features attributed to the N 1s core level and N *KLL* Auger emission, could be observed. Meanwhile, a series of minor peaks attributed to the O 1s core level and the O *KLL* Auger emission could also be detected in the XPS wide-range spectra, likely

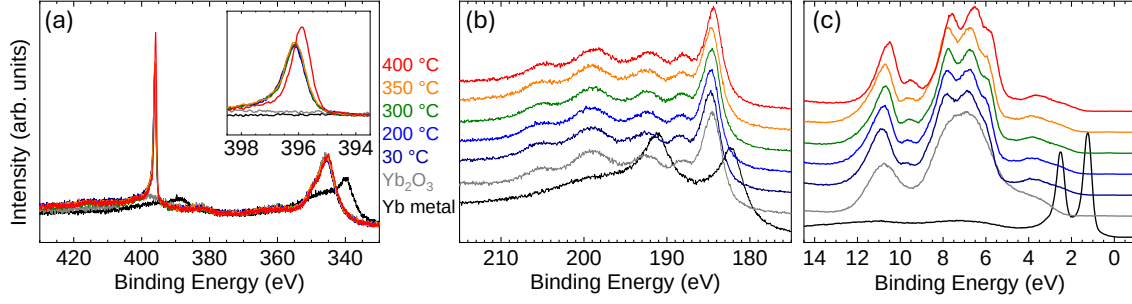


Figure 3.7: Substrate-temperature dependence of the XPS spectrum of YbN thin films and corresponding spectra of Yb_2O_3 (gray) and Yb metal (black). (a) Yb 4*p* and N 1*s* spectra normalized to the integrated area of the corresponding Yb 4*d* core level. The inset shows the spectra zoomed in on the N 1*s* region. (b) Yb 4*d* spectra normalized to their highest peak. (c) Valence band spectra normalized to their highest peak. Each spectrum is shifted upward for clarity in (b) and (c). The spectra of Yb_2O_3 are shifted by -1.7 eV, aligning the Yb 4*d* core level with that of the YbN film grown at 400 °C, to compensate for the charging effect during XPS measurements.

originating from oxidation during the XPS measurements, even in a UHV environment. Evidence of oxidation during the XPS measurement will be provided later. Besides the features mentioned above, no other peaks from contamination could be observed.

Further detailed XPS results of the core levels and valence band are shown in Fig. 3.7. For comparison, the spectrum of a Yb metal film, in which Yb ions are predominantly divalent, together with the spectrum of a Yb_2O_3 film, in which the Yb ions are trivalent, is shown in the same figures. Since Yb_2O_3 is known as a good insulator, a significant charging effect, i.e., a shift of the whole XPS spectrum toward higher binding energy compared with all YbN films, was observed. To compensate for this energy shift due to the charging effect, the spectra of Yb_2O_3 were shifted -1.7 eV in binding energy to align the peak positions of Yb 4*d* core level and Yb 4*f*¹² multiplets to those of the YbN thin film grown at $T_{\text{sub}} = 400$ °C.

The spectra of the energy range including N 1*s* and Yb 4*p* are shown in Fig. 3.7 (a). The sharp peak at approximately 396 eV corresponds to the N 1*s* core level, which overlaps with the Yb 4*p*_{1/2} peak. This makes it difficult to subtract the background of the N 1*s* core level, and thus difficult to calculate the exact Yb/N ratio of the fabricated thin films using the areas of the Yb 4*d* and N 1*s* core levels.

To examine the N 1*s* core level in more detail, the spectra in the N 1*s* region are expanded and shown in the inset of Fig. 3.7 (a). The spectra are normalized to the integrated area of

the corresponding Yb 4*d* core level, allowing a quantitative comparison of the N 1*s* intensities and thus the Yb/N ratios of the different films without deriving the exact area of the N 1*s* core level. One can easily find that the N 1*s* peak retains nearly the same intensity, shape, and binding energy position in samples grown at substrate temperature up to 350 °C. This indicates that the nitrogen content remains unchanged for these films. In contrast, for the sample grown at $T_{\text{sub}} = 400$ °C, the N 1*s* peak shows higher intensity and a sharper shape, suggesting a slightly higher nitrogen concentration and thus fewer nitrogen vacancies in the film. Meanwhile, the energy position of the N 1*s* peak shifts by approximately 0.25 eV toward lower binding energy. A similar shift to lower binding energy with the same value to lower binding energy is observed for all other XPS peaks, i.e., the entire spectrum, as also partly shown in Fig. 3.7 (b) and (c). This indicates that the Fermi level of the sample synthesized at 400 °C undergoes a downward shift relative to that of films grown at lower substrate temperatures. A similar energy shift was also observed in the thin films grown on LaAlO₃ substrates at high substrate temperatures, which will be shown later. Given that the nitrogen vacancies, i.e., the inefficiency of N³⁻ ions that collect the electrons in the *REN* system, act as electron donors [40], one may speculate that this shift of the Fermi level can be attributed to the reduced electron doping of the films grown at the highest substrate temperature because of its highest nitrogen content, and thus would lower the Fermi level.

From the RHEED and XPS results shown above, we can conclude that, with activated nitrogen supplied by the RF plasma sources, YbN thin films can grow on MgO(100) substrates at substrate temperatures ranging from room temperature to 400 °C. Epitaxial growth of YbN layers could be only achieved at $T_{\text{sub}} > 300$ °C, while the chemical components remained almost the same up to a substrate temperature of 350 °C. Meanwhile, the YbN thin film fabricated at the highest substrate temperature ($T_{\text{sub}} = 400$ °C) exhibits sharper streaks in the RHEED pattern together with enhanced N 1*s* peak in XPS, suggesting a better crystal quality as well as a higher nitrogen content. This indicates that the highest substrate temperature is the optimal condition for growing YbN thin films on MgO(100) substrates.

3.3.1.2 Optimization of Yb flux rate

We then began to optimize the Yb flux rate. The Yb flux rate was varied from 3 to 10 Å/min, while the other growth parameters were fixed at a substrate temperature of 400 °C, which

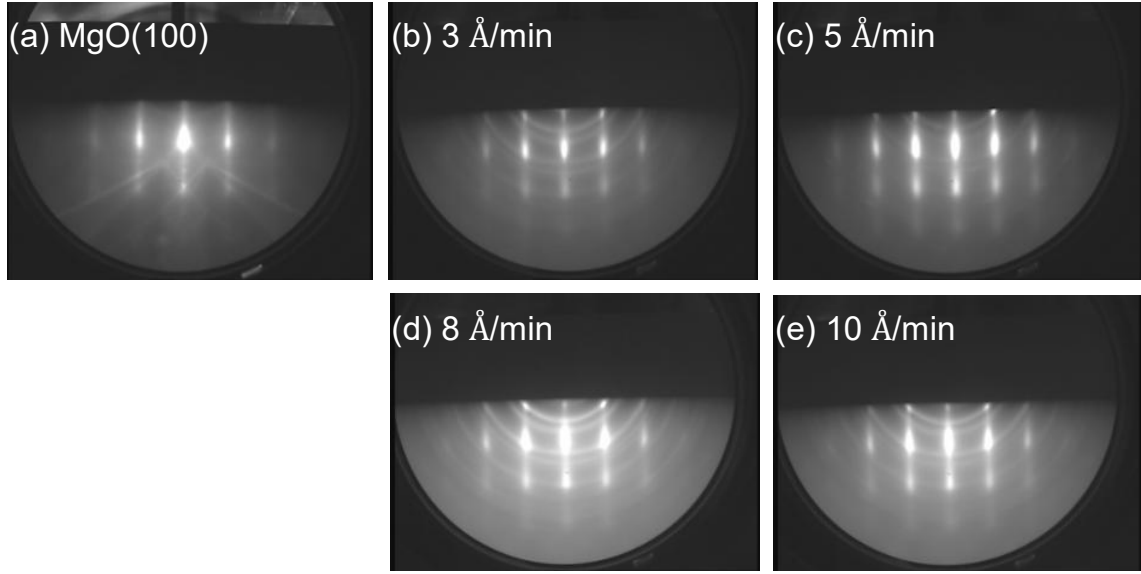


Figure 3.8: Yb-flux-rate dependence of the *in situ* RHEED image of (a) the MgO(100) substrate cleaned by annealing in O₂ atmosphere and of (b-e) YbN films grown at substrate temperature of 400 °C, RF plasma-source power of 100 W, and nitrogen flow of 0.1 SCCM. The incident electron beam was aligned parallel to the [001] crystallographic direction of the MgO(100) substrate.

is the optimal temperature derived from the previous discussion, a plasma-source power of 100 W, and a nitrogen flow of 0.1 SCCM.

Figure 3.8 shows the RHEED patterns of a series of thin films fabricated at different Yb flux rates and at the growth conditions mentioned above. Similar streaks with intensity modulation were observed in all the films grown at different Yb flux rates, indicating that the epitaxial growth occurred on a stepped surface. Meanwhile, we observe that the ring-like features are almost negligible in the film grown with a Yb flux rate of 5 Å/min, but become apparent in films grown at higher or lower Yb flux rates. This suggests that the film fabricated at 5 Å/min exhibits a slightly better-ordered surface than films grown at other rates, indicating that 5 Å/min is the optimal Yb flux rate.

The origin of the enhanced surface disorder of the films grown at Yb flux rates that are higher or lower than the optimal value could be explained as follows: For a lower growth rate, the Yb supply is even less sufficient, and the growth rate of the film is lower. This enhanced influence from the sputtering effect of the nitrogen plasma leads to a slight increase in surface disorder. For a higher growth rate, the fast growth rate results in a slightly degraded surface.

Figure 3.9 exhibits the wide range XPS spectra of the films mentioned above, grown at

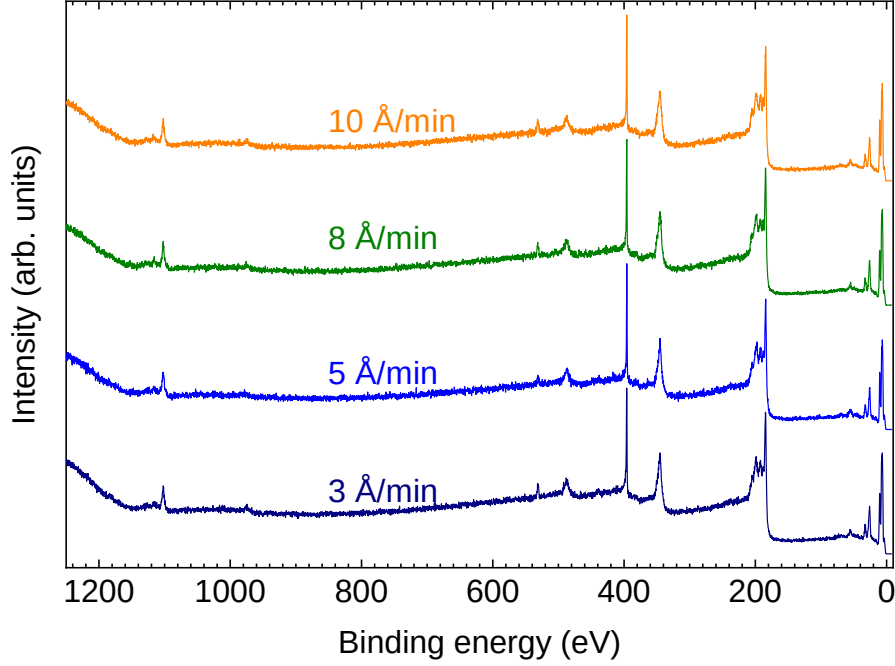


Figure 3.9: Yb-flux-rate dependence of the XPS wide range spectrum of the YbN thin films grown on MgO(100) substrates at the RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, and substrate temperature of 400 °C. Each spectrum is shifted upward for clarity.

different Yb flux rates on MgO(100) substrates. All spectra are generally comparable, and despite peaks from Yb, N, and O, no signals from other contaminants were detected.

Further detailed XPS results of the films, together with those of Yb-metal and Yb₂O₃ films for reference, are shown in Fig. 3.10. The spectra of the films exhibit significant similarity to each other in the Yb 4*p* + N 1*s*, Yb 4*d*, core levels, and valence band, indicating that the films are nearly identical in chemical composition and electronic state. We notice that the film grown at a Yb flux rate of 5 Å/min, i.e., the same sample as that was grown at 400 °C in Fig. 3.7, exhibits a slightly higher intensity and a shift of approximately -0.1 eV, as shown in Fig. 3.10 (a) and its inset. Similar to that discussed in 3.3.1.1, this indicates a comparatively higher nitrogen concentration in the film grown at 5 Å/min, consistent with the optimal Yb flux rate derived from the RHEED patterns. Meanwhile, comparing with the intensity difference and the amount of energy shift between the film grown at the highest substrate temperature and those of other films grown at lower temperatures, as shown in Fig. 3.7, the intensity difference and energy shift between films grown at an optimal Yb flux rate of 5 Å/min and other Yb flux rates are comparatively small. This suggests that the Yb flux rate is less important than the substrate temperature for the growth of epitaxial

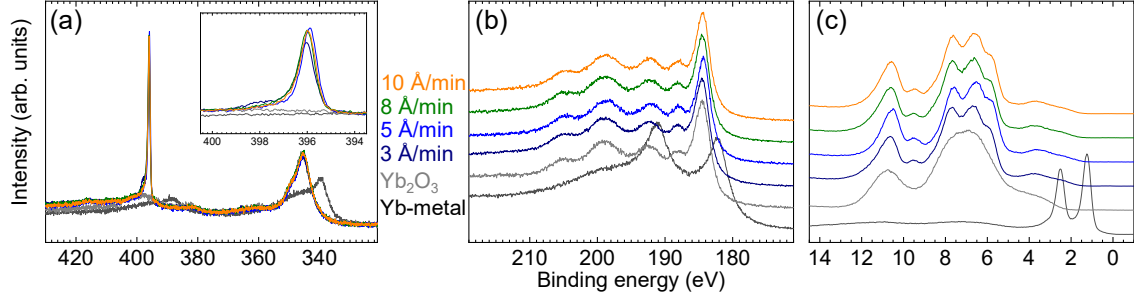


Figure 3.10: Yb-flux-rate dependence of the XPS spectrum of YbN thin films grown on MgO(100) substrates and corresponding spectra of Yb₂O₃ (gray) and Yb metal (black). (a) Yb 4p and N 1s spectra normalized to the integrated area of the corresponding Yb 4d core level. The inset shows the spectra zoomed in the N 1s region. (b) Yb 4d spectra normalized to their highest peak. (c) Valence band spectra normalized to their highest peak. Each spectrum is shifted upward for clarity in (b) and (c). The spectra of Yb₂O₃ are shifted by -1.7 eV, aligning the Yb 4d core level with that of the YbN film, to compensate for the charging effect during XPS measurements.

and stoichiometric YbN thin films. Also, unlike the films fabricated at the Yb flux rate varying from 5 Å/min to 10 Å/min exhibit only one N 1s peak with similar intensity at approximately 396 eV, the film fabricated at 3 Å/min shows a main N 1s peak which is weaker compared with those of films grown at a higher rate, at around 396 eV, together with a shoulder-like structure at around 398 eV. This shoulder-like structure is considered to originate from a satellite peak of the N 1s core level, which can be attributed to nitrogen in a different chemical environment, resulting from the defect introduced by plasma-induced sputtering.

From the discussion above and in Section 3.3.1.1, we could draw a conclusion that the Yb flux rate of 5 Å/min and a substrate temperature of 400 °C are the optimal growth conditions for YbN thin films on MgO (100) substrate.

3.3.2 Optimization of the growth conditions on LaAlO₃(100)

A similar optimization process of the growth conditions to that mentioned in Section 3.3.1 has also been conducted for the growth of YbN thin film on LaAlO₃ (001) substrates.

Figure 3.11 shows the RHEED patterns of a series of samples grown on LaAlO₃ substrate at a Yb flux rate of 2 Å/min, plasma power of 100 W, and nitrogen flow rate of 0.1 SCCM. Consistent with the substrate temperature dependence of RHEED patterns of YbN films

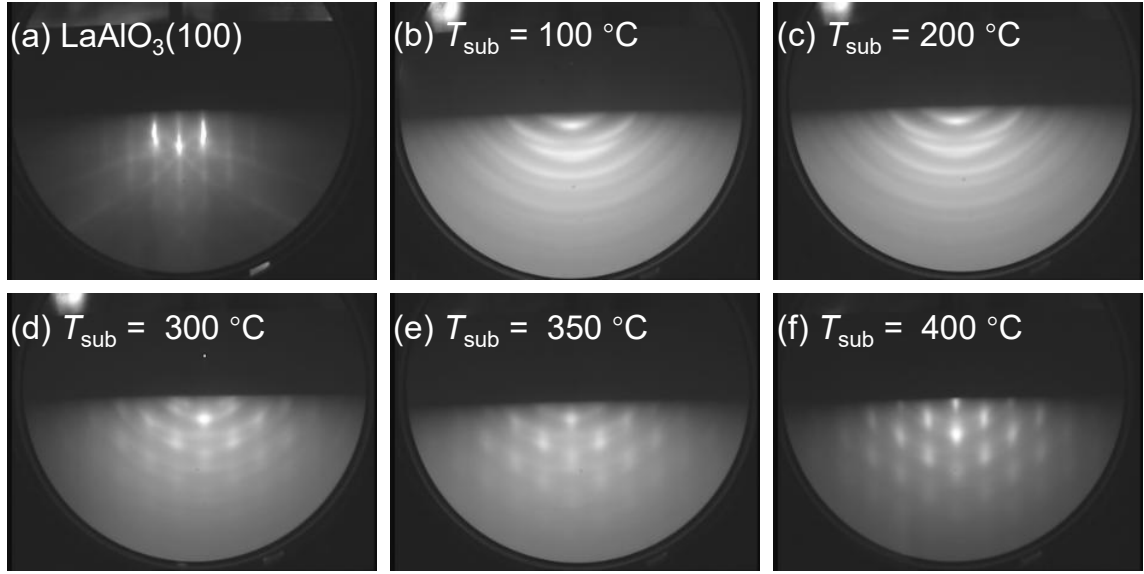


Figure 3.11: Substrate-temperature dependence of the *in situ* RHEED image of (a) the $\text{LaAlO}_3(100)$ substrate cleaned by annealing in O_2 atmosphere and of (b-f) YbN films grown at Yb flux rate of $2 \text{ \AA}/\text{min}$, RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, and indicated substrate temperatures. The incident electron beam was aligned parallel to the $[001]$ crystallographic direction of the $\text{LaAlO}_3(100)$ substrate.

grown on $\text{MgO}(100)$, as shown in Fig. 3.8, Higher substrate temperature results in better RHEED patterns and thus better crystalline quality of the film: At a substrate temperature below $200 \text{ }^\circ\text{C}$, only ring-like structures appear in the RHEED pattern, indicating the polycrystallinity of the sample surface. When $T_{\text{sub}} = 300 \text{ }^\circ\text{C}$, fuzzy transmission spots appear, and the intensity of the ring-like structure is weakened, suggesting a mixed growth mode of polycrystal and three-dimensional growth. Ring-like features become fainter as the substrate temperature increases, along with more pronounced transmission spots and a lower background, indicating improved crystal quality. At $400 \text{ }^\circ\text{C}$, streak-like features start to appear, and the ring-like features become negligible, although still comparatively spotty, suggesting the formation of an epitaxial surface with comparatively strong three-dimensional features.

Compared to the RHEED patterns of the YbN films on $\text{MgO}(100)$ substrates shown in Fig. 3.5, the YbN films grown on LaAlO_3 exhibit RHEED patterns with a different appearance and spacing. This difference is considered to originate from the fact that the YbN layers show a 45° in-plane-rotated growth on $\text{LaAlO}_3(100)$ and grow on $\text{MgO}(100)$ without any in-plane rotation. The lattice parameter is calculated to be $3.33 \pm 0.06 \text{ \AA}$ by comparing the spacing of RHEED patterns of the synthesized film with that of the RHEED pattern of

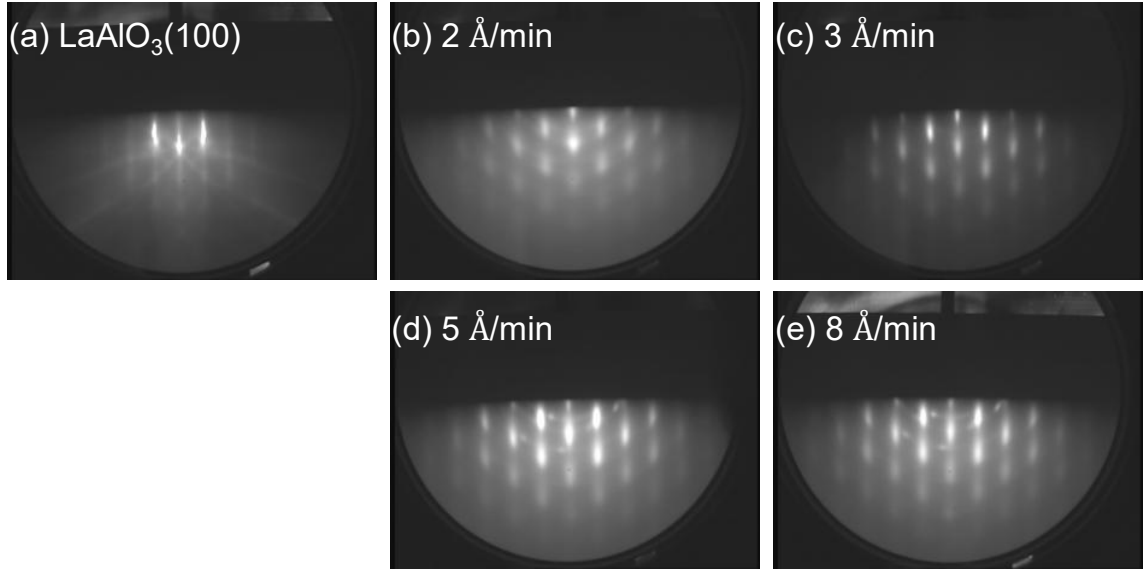


Figure 3.12: Yb-flux-rate dependence of the *in situ* RHEED image of the YbN films grown on $\text{LaAlO}_3(100)$ at a substrate temperature of 400 °C, RF plasma-source power of 100 W, and nitrogen flow of 0.1 SCCM. The incident electron beam was aligned parallel to the [001] crystallographic direction of the $\text{LaAlO}_3(100)$ substrate.

$\text{LaAlO}_3(100)$ substrate. This corresponds to a lattice parameter of 4.71 ± 0.08 Å taking the 45° in-plane rotation into account, which is consistent with the reported bulk value of YbN [68] and the value (4.785 Å) derived from the RHEED patterns of the YbN films grown on $\text{MgO}(100)$.

One would also notice that the quality of the films grown on $\text{LaAlO}_3(100)$ surfaces is inferior to that of the films grown on $\text{MgO}(100)$ substrates at the same substrate temperature. This could be attributed to plasma-induced sputtering, resulting from a low growth rate caused by a Yb flux rate below the optimal value.

Figure 3.12 shows the RHEED patterns grown on $\text{LaAlO}_3(100)$ substrates at a substrate temperature of 400 °C and different Yb flux rates. One can readily point out that the RHEED pattern of the film grown at a Yb flux rate of 3 Å/min shown in Fig. 3.12 (b) exhibits the most crisp streaks together with the faintest additional ring-like or dot-like structures that suggest the minor disorder of the surface. At a lower Yb flux rate of 2 Å/min, the streaks are weaker and broader; also, a more spot-like shape of the diffraction patterns suggests a more three-dimensional surface. This could be attributed to increased plasma-induced sputtering due to the longer growth time resulting from a lower Yb flux rate than the optimal value. For the films grown at a higher Yb flux rate, clear streaks with intensity

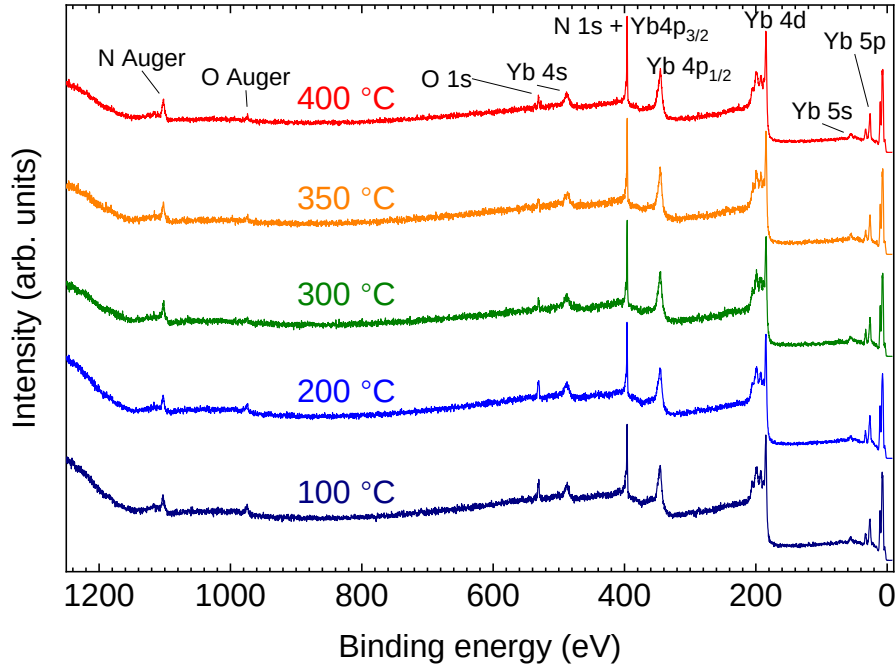


Figure 3.13: Substrate-temperature dependence of the XPS wide range spectrum of the YbN thin films grown on $\text{LaAlO}_3(100)$ substrates at the RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, and Yb flux rate of $2 \text{ \AA}/\text{min}$. Each spectrum is shifted upward for clarity.

modulation are also observed in RHEED, while additional spot- and ring-like structures are intensified, indicating increasing surface disorder, possibly due to a growth rate higher than optimal. This tendency is similar to that of the growth of YbN thin films on $\text{MgO}(100)$ substrates discussed in Section 3.3.1.2.

Figures 3.13 and 3.14 show the XPS wide-range scans of the YbN thin films grown on $\text{LaAlO}_3(100)$ substrate with varying substrate temperatures and varying Yb flux rate. As discussed in Figs. 3.6 and 3.9, all the detected peaks originate from N, Yb, or O, while no other contaminations are observed. The films grown at $100 \text{ }^\circ\text{C}$ and $200 \text{ }^\circ\text{C}$ and a Yb flux rate of $2 \text{ \AA}/\text{min}$ show slightly lower intensity of N $1s$ core level and slightly intensified O $1s$ and O KLL Auger emission, possibly related to the bad crystallinity (Fig. 3.11) because of the oxidation and plasma-induced sputtering due to the low substrate temperature and slow growth rate. Except for that, other spectra in Figs. 3.13 and 3.14 are generally comparable.

Detailed XPS spectra of the above-mentioned films are shown in Figs. 3.15 and 3.16. For the dependence on Yb flux rate, YbN films grown at $5 \text{ \AA}/\text{min}$ and $9 \text{ \AA}/\text{min}$ show a slightly

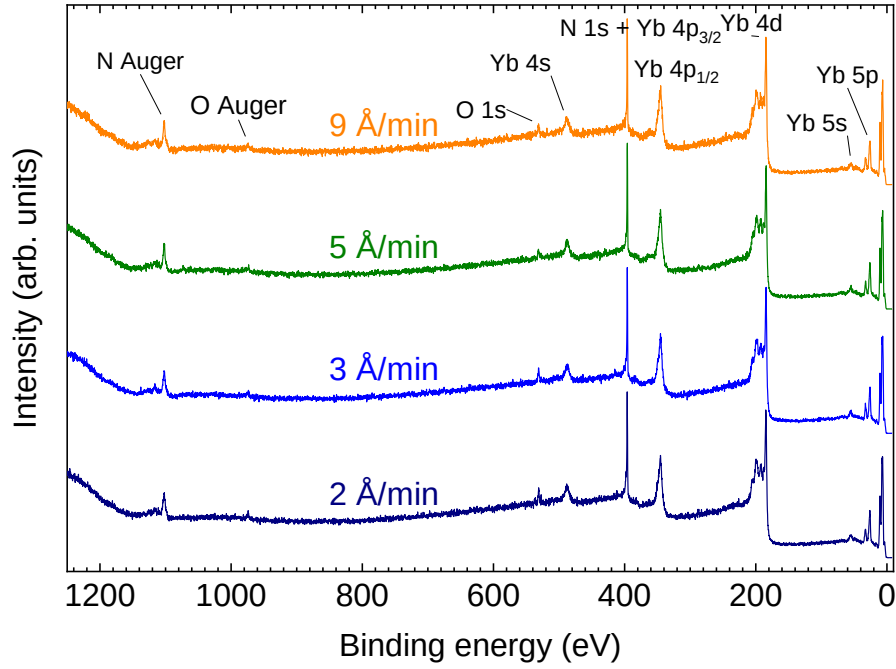


Figure 3.14: Yb-flux-rate dependence of the XPS wide range spectrum of the YbN thin films grown on $\text{LaAlO}_3(100)$ substrates at the RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, and substrate temperature of 400 °C. Each spectrum is shifted upward for clarity.

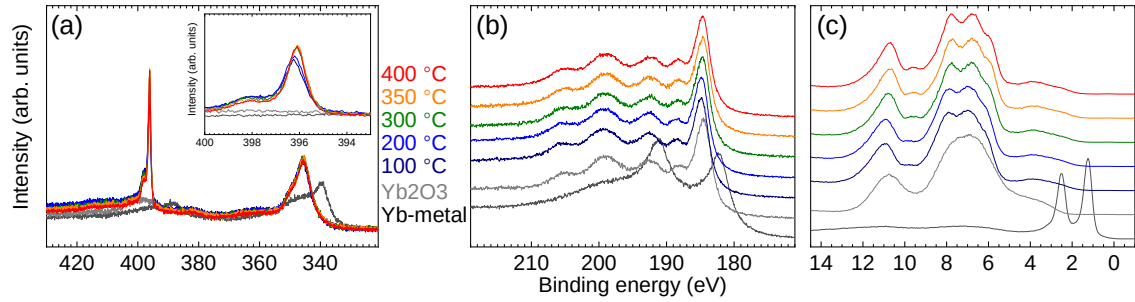


Figure 3.15: Substrate-temperature dependence of the XPS spectrum of YbN thin films grown on $\text{LaAlO}_3(100)$ substrates with the constant Yb flux rate of 2 Å/min, and corresponding spectra of Yb_2O_3 (gray) and Yb metal (black). (a) Yb 4p and N 1s spectra normalized to the integrated area of the corresponding Yb 4d core level. The inset shows the spectra zoomed in on the N 1s region. (b) Yb 4d spectra normalized to their highest peak. (c) Valence band spectra normalized to their highest peak. Each spectrum is shifted upward for clarity in (b) and (c). The spectra of Yb_2O_3 are shifted by -1.7 eV, aligning the Yb 4d core level with that of the YbN film grown on $\text{MgO}(100)$ substrate at 400 °C and 5 Å/min, to compensate for the charging effect during XPS measurements.

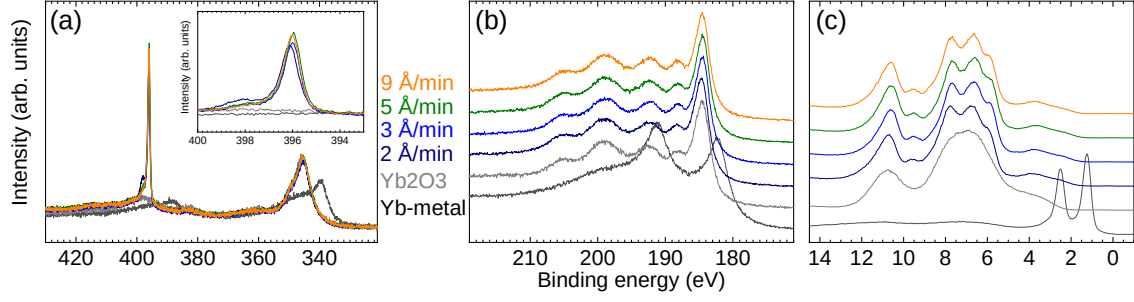


Figure 3.16: Yb-flux-rate dependence of the XPS spectrum of YbN thin films grown on $\text{LaAlO}_3(100)$ substrates at a constant substrate temperature of 400°C , and the corresponding spectra of Yb_2O_3 (gray) and Yb metal (black). (a) Yb $4p$ and N $1s$ spectra normalized to the integrated area of the corresponding Yb $4d$ core level. The inset shows the spectra zoomed in on the N $1s$ region. (b) Yb $4d$ spectra normalized to their highest peak. (c) Valence band spectra normalized to their highest peak. Each spectrum is shifted upward for clarity in (b) and (c). The spectra of Yb_2O_3 are shifted by -1.7 eV, aligning the Yb $4d$ core level with that of the YbN film grown on $\text{MgO}(100)$ substrate at 400°C and $5 \text{ \AA}/\text{min}$, to compensate for the charging effect during XPS measurements.

higher intensity of the N $1s$ core level than those grown at $2 \text{ \AA}/\text{min}$ or $3 \text{ \AA}/\text{min}$, indicating an increased nitrogen content for a comparatively high deposition rate. Meanwhile, all the films grown at a Yb flux rate of $2 \text{ \AA}/\text{min}$ (all curves in Fig. 3.15 and the purple curve in Fig. 3.16), which is considered lower than the optimal value, show a clear satellite feature at around 398 eV, while the films grown at a higher Yb flux rate not, which is consistent with the result of the films grown on $\text{MgO}(100)$ substrates discussed in Section 3.3.1.2. Therefore, the origin of the satellite features is considered to be related to surface defects resulting from the enhanced effect of plasma-induced sputtering, which occurs due to the low growth rate. Similarly, as shown in Fig. 3.15 (a), while the films grown at a substrate temperature lower than 200°C show a lower intensity of the main peak of N $1s$ core level at approximately 396 eV, the main N $1s$ peak is comparatively intensified for the films grown at a substrate temperature higher than 300°C , together with a shift of the whole spectrum for approximately 0.15 eV to the lower binding energy side. Although the exact substrate temperature where the changes happen and the size of the energy shift are different from those of the films grown on $\text{MgO}(100)$, the general tendency is similar, suggesting that higher substrate temperature also leads to better nitrogen stoichiometry, as previously discussed in Section 3.3.1.2.

From the RHEED and XPS results discussed, the optimal substrate temperature and

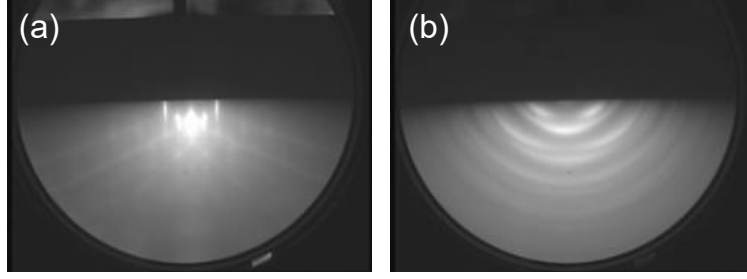


Figure 3.17: RHEED patterns of a $\text{YVO}_4(001)$ clean surface measured just before growth (a), and YbN thin film deposited on the $\text{YVO}_4(001)$ substrate measured just after growth.

Yb flux rate for the growth of epitaxial YbN thin films on LaAlO_3 are determined to be 400°C and $3 \text{ \AA}/\text{min}$ or $5 \text{ \AA}/\text{min}$.

3.3.3 Attempt to grow YbN thin film on $\text{YVO}_4(001)$

As introduced in Section 3.1.1, the lattice parameter of $\text{YVO}_4(001)$ is $7.12 \text{ \AA}$, which could be considered as an effective lattice parameter of $5.04 \text{ \AA}$. Therefore, YVO_4 exhibits the smallest lattice mismatch among the three substrates used in our study, compared with YbN, which is a factor that could possibly facilitate epitaxial growth of YbN.

However, our attempt to grow epitaxial YbN on $\text{YVO}_4(100)$ proved unsuccessful. Figure 3.17 shows the RHEED pattern of a thin film sample grown on $\text{YVO}_4(001)$ substrate at a substrate temperature of 400°C , Yb flux rate of $3 \text{ \AA}/\text{min}$, plasma-source power of 100 W , and nitrogen flow of 0.1 SCCM . Given that RHEED patterns with intensity-modulated streaks that suggest an epitaxial surface with several surface steps were observed in the films grown on both $\text{MgO}(100)$ and $\text{LaAlO}_3(100)$ substrates under the same growth conditions, the observed ring-like structures and thus the indicated polycrystallinity of the thin film suggest that $\text{YVO}_4(001)$ is less capable for the growth of epitaxial YbN layers.

The chemical composition of the film fabricated on $\text{YVO}_4(001)$ was further analyzed by XPS. The XPS wide range spectra of the YbN film grown on $\text{YVO}_4(001)$ is shown in Fig. 3.18, together with that of a film grown on $\text{MgO}(100)$ substrate at the optimal conditions (Yb flux rate of $5 \text{ \AA}/\text{min}$ and substrate temperature of 400°C) for comparison. One can readily find that the two spectra share the same series of peaks attributed to Auger emissions and core levels of Yb, N, and O. Meanwhile, we noticed that the film grown on YVO_4 exhibits stronger peaks of O $1s$ and O KLL Auger emission, which could possibly

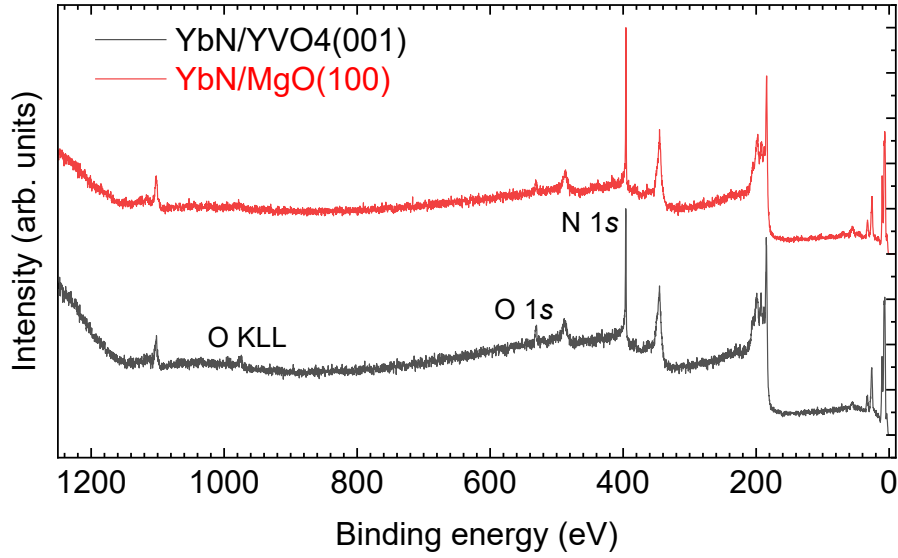


Figure 3.18: XPS wide range spectra of a YbN thin film grown on $\text{YVO}_4(100)$ substrate at the RF plasma-source power of 100 W, nitrogen flow of 0.1 SCCM, Yb flux rate of $3 \text{ \AA}/\text{min}$, and substrate temperature of $400 \text{ }^\circ\text{C}$ (black). The spectrum of a YbN film grown on $\text{MgO}(100)$ at optimal conditions is shown in red for comparison.

not be attributed completely to the oxidation process during the XPS measurement, as that would be discussed in Section 3.3.6. The origin of the increased oxygen concentration in the film can be attributed to oxidation by oxygen lost from the YVO_4 substrate at a high substrate temperature. One can also point out that the intensity of the sharp N 1s peak at approximately 396 eV of the film grown on $\text{YVO}_4(001)$ is relatively lower than that of the film grown on $\text{MgO}(100)$, suggesting a comparatively lower nitrogen content.

From the RHEED and XPS results discussed above, we could draw a conclusion that $\text{YVO}_4(001)$ is not as good as $\text{MgO}(100)$ or $\text{LaAlO}_3(100)$ as a substrate for the growth of epitaxial and stoichiometric YbN thin films, despite its better lattice matching to YbN.

3.3.4 The influence of plasma-source power and nitrogen flow

In the previous report on MBE growth of epitaxial REN thin films with molecular nitrogen, when the flux rate of RE and the substrate temperature are fixed, a higher nitrogen pressure leads to a better crystalline quality, as well as a higher nitrogen content and fewer nitrogen vacancies [40, 43]. Therefore, we attempted to grow YbN films with a higher nitrogen flow and plasma-source power to determine whether this approach is also applicable for MBE growth using an RF plasma source.

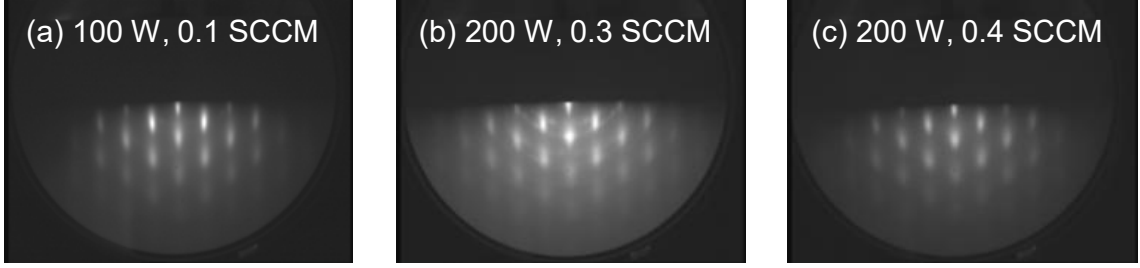


Figure 3.19: Plasma-source-power and nitrogen-flow-rate dependence of *in situ* RHEED image of a series of samples grown on $\text{LaAlO}_3(100)$ substrate, at a Yb flux rate of $3 \text{ \AA}/\text{min}$, and substrate temperature of $400 \text{ }^\circ\text{C}$. (a) 100 W, 0.1 SCCM, (b) 200 W, 0.3 SCCM, and (c) 200 W, 0.4 SCCM.

Figure 3.19 shows the RHEED patterns of a series of samples grown on $\text{LaAlO}_3(100)$ at a substrate temperature of $400 \text{ }^\circ\text{C}$, Yb flux rate of $3 \text{ \AA}$, and at different sets of plasma-source power and nitrogen flow. For the film grown at 100 W and 0.1 SCCM, as shown in Fig. 3.19 (a), a RHEED pattern with intensity-modulated streaks was observed, suggesting an epitaxial surface with several steps. The films grown at higher plasma-source power and Yb flux rate show basically similar RHEED patterns, as shown in Figs. 3.19 (b) and (c). However, the streaks are weaker when transmission-spot-like features are stronger, suggesting a more three-dimensional growth of these films compared to that grown at low plasma-source power and Yb flux rate. Meanwhile, the additional ring-like features also become more apparent, especially in Fig. 3.19 (b), indicating a more disordered surface. This suggests that the plasma-source power of 100 W and a Yb flux rate of 0.1 SCCM are the optimal conditions for the growth of YbN epitaxial layers.

The result that more supplied nitrogen leads to degraded crystallinity seems to be the opposite of the growth of REN thin films with molecular nitrogen. This could be explained as follows: For the growth of REN with molecular nitrogen, although the RE atoms could catalytically break the N_2 molecules, the reactivity between RE atoms and N_2 is limited. Therefore, increasing nitrogen pressure results in more N_2 molecules participating in the reaction, thereby suppressing the generation of nitrogen vacancies and facilitating the formation of higher-quality crystals. On the other hand, for the growth of YbN thin films with the RF plasma source in this work, the reactivity of the radical nitrogen provided from the plasma source is much more enhanced compared to the catalytic reaction of molecular nitrogen with rare-earth atoms. This leads to an excessive nitrogen supply during YbN growth, even with a relatively higher Yb flux rate and lower nitrogen supply. (Nitrogen

flow of 0.43 SCCM is needed for a pressure of 1×10^5 mbar of molecular nitrogen.) As a result, the increasing nitrogen supply would not increase the chance of the reaction between nitrogen and Yb atoms in this work. In contrast, the increasing plasma power enhanced the plasma-induced sputtering, which leads to a slightly rougher surface with increasing surface disorder.

3.3.5 Comparison of the characteristics between the plasma-assisted growth of YbN thin films and the growth of *REN* thin films with molecular nitrogen

From Section 3.3.1, 3.3.2, and 3.3.4, we drew a conclusion that epitaxial YbN thin films could be synthesized on both MgO(100) and LaAlO₃(100) substrates. The optimal growth condition was determined to be a substrate temperature of 400 °C, a plasma power of 100 W, a nitrogen flow of 0.1 SCCM, and a Yb flux rate of around 3-5 Å.

It is noteworthy that the characteristics of the growth of YbN thin films with RF nitrogen plasma sources differ significantly from those of the growth of other *REN* thin films using molecular nitrogen.

In previous studies on various *REN* thin films grown with molecular nitrogen supply, it is suggested that the higher substrate temperatures favor the formation of nitrogen vacancies, while lower growth rate and higher N₂ pressure lead to a better ordered surface and better stoichiometry [5, 39, 40, 43, 135, 136].

However, the situation is different for the growth of YbN in this study with the nitrogen plasma source. For the substrate temperature, YbN films grown on MgO(100) substrates exhibit an even higher and sharper N 1s peak for the film grown at a high substrate temperature of 400 °C as shown in Fig. 3.7 (a), indicating a better nitrogen stoichiometry. Furthermore, the YbN films grown at such a high substrate temperature show no signs of degradation in crystallinity (Fig. 3.5) or oxidation (Fig. 3.6) compared to the films grown at lower substrate temperatures. Similar results are also observed on the films grown on LaAlO₃ (100) substrates, suggesting that they are not due to any randomness or unique characteristic of the MgO(100) substrates. These observations contrast with a study on HoN thin films grown with molecular nitrogen [43], where clearly increased oxygen content, decreased nitrogen content, and degraded RHEED were observed when grown at comparable high substrate temperatures.

Moderate growth rates are well known as one of the facts that facilitate the epitaxial layer-by-layer growth for the synthesis of thin-film samples with MBE. In the reported growth of *REN* thin films, a low *RE* flux rate of approximately 1 Å/min was favored for the growth of stoichiometric and epitaxial *REN* layers [40, 43]. In contrast, in this study, such a low Yb flux rate leads to a degraded RHEED pattern, while a comparatively higher value is preferred, as shown in sections 3.3.1 and 3.3.2.

For the nitrogen pressure, while a higher nitrogen pressure of 5×10^{-5} mbar leads to a better growth results and a higher tolerances for a high substrate temperatures for the growth of *REN* with molecular nitrogen [40, 43], the increasing of nitrogen supply with the RF plasma source only results in a degraded crystal quality.

These differences can be attributed to the enhanced reactivity of radical nitrogen from the RF plasma source compared to the catalytic reaction of molecular nitrogen with rare-earth atoms, as well as to the sputtering effect on the sample surfaces induced by the nitrogen plasma. As already discussed in Section 3.3.1 and 3.3.4, comparatively high Yb flux rates, low plasma power, and low nitrogen flow are favored in the sense of suppressing the degradation due to the plasma-induced sputtering effect by limiting the plasma power and shortening the growth time, giving the nitrogen supply is always excessive because of the high reactivity.

For the high quality of the samples grown at high substrate temperature, a similar discussion could also be applied: The highly reactive radical nitrogen from the RF plasma source ensures the excessive nitrogen supply during YbN growth in this study. As a result of the nitrogen excess condition, almost all Yb atoms deposited onto the substrate surfaces preferentially react with the radical nitrogen, which suppresses not only the revaporation of the Yb atoms, but also the degradation because of the oxidation by the small amount of residual oxygen in the UHV chamber or the oxygen lost from the oxygen-containing MgO(100) and LaAlO₃(100) substrates at high temperature.

The presence of nitrogen could be further confirmed by the following fact: As shown in Figs. 3.7 and 3.8, when the substrate temperature was increased from room temperature to 350 °C, which is already clearly above the distillation temperature of elemental ytterbium at the deposition position, the composition and electronic structure of the YbN films grown on MgO(100) substrates remained nearly unchanged despite the significant improvement of the crystalline quality. This is also applicable even for a doubled Yb flux rate of 10 Å, as

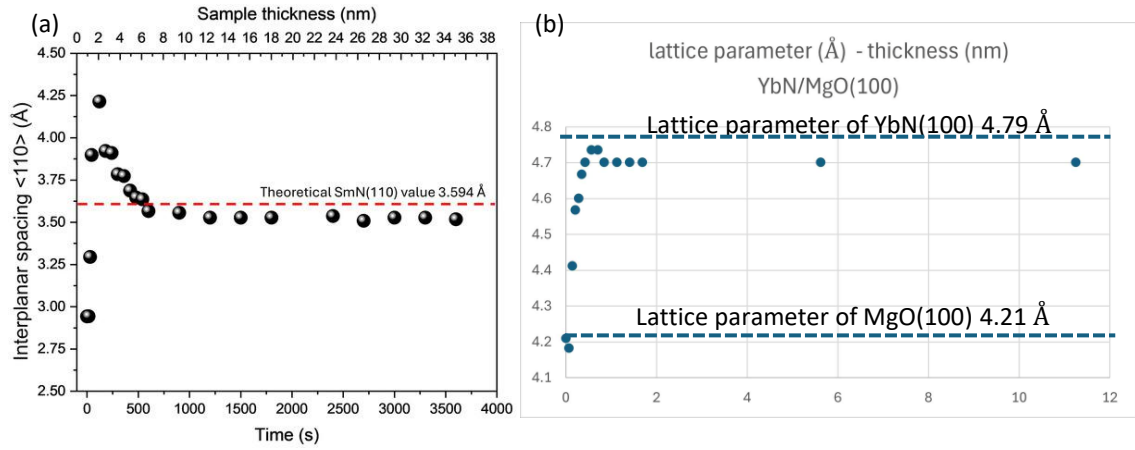


Figure 3.20: (a) Development of the interplanar spacing depending on the thickness during the growth of SmN(100) epitaxial thin film on MgO(100) substrate with molecular nitrogen, reported in Ref. [41]. (b) Development of surface lattice parameter depending on the thickness during the growth of YbN(100) epitaxial thin film at substrate temperature of 400 °C with plasma-assisted MBE derived from the RHEED pattern measured in real time during the growth.

shown in Figs. 3.8 and 3.10. These results suggest that all the ytterbium atoms deposited on the substrate surfaces reacted with radical nitrogen to form YbN, thus confirming the excess nitrogen.

The effects of highly reactive nitrogen species supplied by the nitrogen plasma source and the nitrogen-excess condition are also clearly evident in the different relaxation behavior of the lattice mismatch in the first few layers.

Figure 3.20 (a) illustrates the interplanar spacing measured from the distance between streaks in the RHEED patterns during the epitaxial growth of SmN(100) epitaxial thin films with molecular nitrogen [41]. During the first 2 nm of growth, the interplanar spacing increased from the value of the MgO(110) to around 4.25 Å, which is much larger than the expected spacing of SmN(110) (3.594 Å). Meanwhile, over the subsequent several nm of growth, the interplanar spacing decreased and gradually saturated to the theoretical value for SmN(110). This growth behavior indicates the formation of the samarium oxides during the growth of the first few layers.

On the other hand, as shown in Fig. 3.20 the lattice parameter of the YbN thin films grown on MgO(100) substrate with nitrogen plasma source in this study, however, the lattice parameter relaxed frequently within the first 0.5 nm of growth to the value of the literature lattice parameter of YbN(100) without over shooting, indicating the formation of

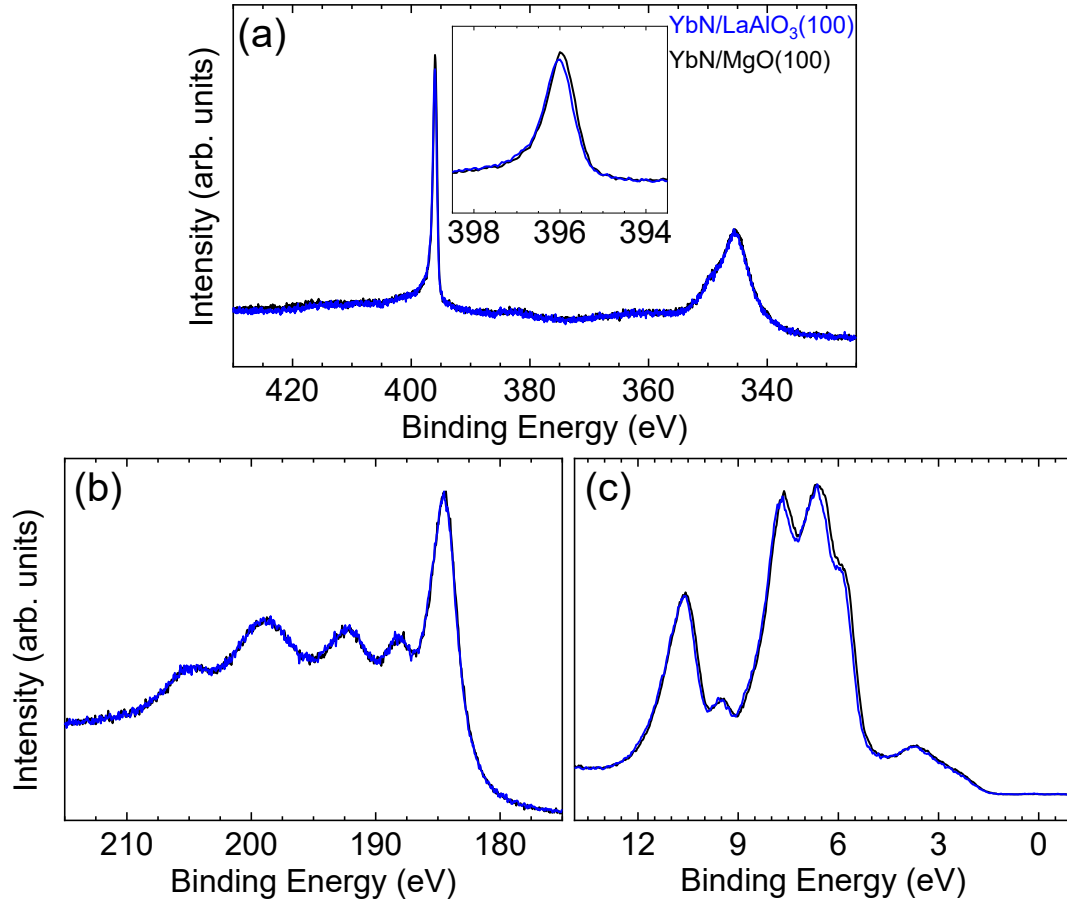


Figure 3.21: XPS spectra measured *in situ* of a sample grown at 400 °C and on a $\text{LaAlO}_3(100)$ substrate (blue), together with the XPS results of a YbN thin film grown on a $\text{MgO}(100)$ substrate under similar conditions (black). (a) Yb 4*p* and N 1*s* core-level spectra. (b) Yb 4*d* core-level spectra. (c) Valence band spectra. The spectra of both samples are generally identical, with no significant difference found.

YbN layers from the very beginning of the growth.

This result suggests the suppression of oxide layer formation, which could be attributed to the higher reaction efficiency between the nitrogen plasma and the deposited ytterbium, even compared with the oxygen loss from the MgO substrate at a comparatively high substrate temperature of 400 °C, resulting in better quality near the interface.

In addition, in previous reports on HoN and SmN thin films, $\text{LaAlO}_3(100)$ has been proven to be a superior substrate to $\text{MgO}(100)$ [40, 43]. On the other hand, in this study, the epitaxial growth of YbN films is demonstrated to be possible on both $\text{MgO}(100)$ and $\text{LaAlO}_3(100)$ substrates, and no clear difference in crystalline quality or electronic structure is observed (3.21). This suggests the similar superiority of $\text{MgO}(100)$ and $\text{LaAlO}_3(100)$ sub-

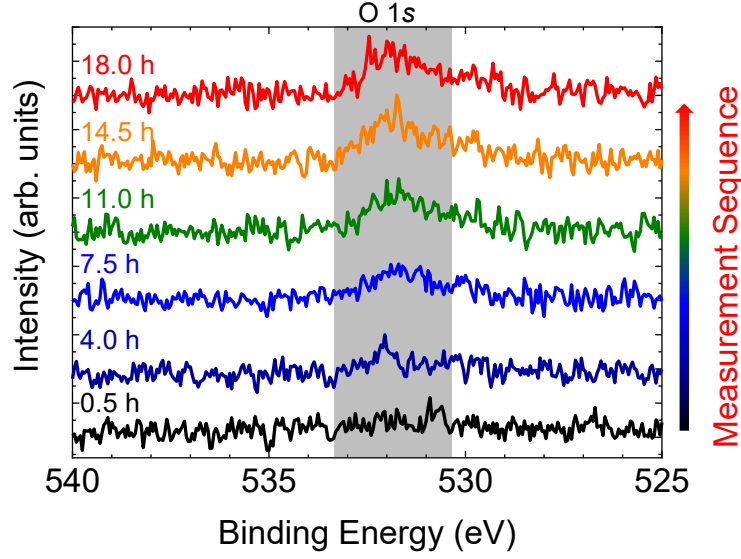


Figure 3.22: Time-dependent O 1s XPS spectra of a YbN thin film grown on a MgO(100) substrate at optimal conditions. For each spectrum, the time after the start of the measurement is indicated. The spectra are shifted upwards in the measurement sequence for clarity.

strates for the plasma-assisted growth of YbN thin film. This difference can be understood as follows: Since Yb is the second-to-last element in the rare-earth elements, YbN exhibits a smaller lattice parameter compared to SmN or HoN, whose lattice parameters are closer to that of LaAlO₃ when a 45° in-plane-rotated growth is considered. As a result, as shown in Section 3.1.1, the value of the lattice mismatch between YbN and MgO(100) LaAlO₃(100) substrates is similar, resulting in similar growth results on the two kinds of substrates.

3.3.6 Oxidation during XPS measurement

In the XPS results for all the YbN thin films mentioned above, a set of minor features corresponding to the O 1s core level and O *KLL* Auger emission could be observed, even though the growth, transfer, and measurement were conducted within a UHV system with a base pressure of about 1×10^{-10} mbar. To investigate the origin of this contamination, we evaluate the time dependence of the XPS measurement.

In order to acquire a moderate signal-to-noise ratio of XPS results, for each synthesized film, six rounds of XPS measurements were performed in the same sequence: wide scan, O 1s, N 1s & Yb 4p, Yb 4d, and valence band. Each full sequence took approximately 3.5 hours to complete. This provides us with the opportunity to trace the oxidation process of the fabricated thin-film samples by analyzing the temporal evolution of the O 1s core-level

spectra.

Figure 3.22 shows the O 1s spectra for each iteration of a YbN film grown on a MgO(100) substrate under the optimized growth condition, i.e., $T_{\text{sub}} = 400$ °C, Yb flux rate of 5 Å/min, plasma-source power of 100 W, and N₂ flow of 0.1 SCCM. In the first scan, measured approximately 0.5 hours after starting the XPS measurement, the O 1s peak was negligible. However, the O 1s peak intensified over time, and could be clearly identified in the spectra measured after 11 hours. This suggests that the oxygen detected in the YbN thin films is at least not completely related to the growth process. Instead, oxidation occurs gradually during the XPS measurement, despite the ultra-clean environment where the measurement was conducted. A similar oxidation process during XPS measurement has also been reported previously for epitaxial HoN thin films grown by MBE with molecular nitrogen supply [43].

3.4 Characterization of the YbN thin films

In this section, we provide a more detailed discussion on the electronic state and crystalline structure of the YbN thin films.

3.4.1 Valence state of Yb ions in YbN thin films

We first look into the valence state of the Yb ions. As shown in Figs. 3.7 (a), 3.10 (a), 3.15 (a), and 3.16 (a), besides the sharp peak near 396 eV attributed to the N 1s core-levels, peaks around 400 and 345 eV are observed. As they closely match those features in the Yb₂O₃ reference film, these features could be assigned to the 4p_{1/2} and 4p_{3/2} core levels of trivalent Yb ions. On the other hand, in the spectrum of the Yb metal sample, where Yb ions are predominantly in the divalent state [133], a different set of features at around 390 eV and 340 eV appears. However, no signal from these features could be observed in the YbN samples.

Similar results are also observed in the Yb 4d core level and the valence band spectra displayed in Figs. 3.7 (b), 3.10 (b), 3.15 (b), and 3.16 (b). In the Yb 4d region, all spectra of YbN films exhibit peaks at around 184.5 eV, 188.2 eV, 192.4 eV, 199 eV, and 205.2 eV, which are similar in shape to that of Yb₂O₃ film, while the features at around 182 eV and 192 eV are absent. In the valence band spectra shown in Figs. 3.7 (c), 3.10 (c), 3.15

(c), and 3.16 (c), the YbN thin films show features similar to the Yb $4f^{12}$ multiplets in the binding energy region from 5 eV to 14 eV, while the YbN thin films show a sharper spectral shape than Yb₂O₃. Additionally, comparatively broad features centered around 3 and 4 eV are observed in the valence band of YbN films and Yb₂O₃ film, respectively, which are attributed to be related to N $2p$ and O $2p$ states. In contrast, sharp Yb $4f^{13}$ doublets at approximately 1.2 and 2.4 eV that are shown in the valence band of Yb metal are also completely absent in all the spectra of the YbN films.

As discussed above, the core level and valence band spectra share a significant similarity in the spectral shape between the YbN films and Yb₂O₃, indicating that Yb ions in the YbN films are in a trivalent state. Meanwhile, no features corresponding to divalent Yb ions could be detected in the spectra of YbN thin films. Given an XPS detection limit down to ~ 1 % concentration of the components, we could exclude the presence of even relatively small amounts of divalent Yb ions. Therefore, the absence of the Yb²⁺ contribution in both the core-level and valence band spectra of the YbN films confirms that the Yb ions are entirely trivalent.

3.4.2 Semiconducting nature and p - f hybridization in YbN thin films

We then discuss the electronic structure of the fabricated YbN thin films in more detail by comparing the valence-band spectra obtained at different photon energies on the same sample.

Figure 3.23 displays the valence band spectra of a YbN sample grown on a MgO(100) substrate measured by XPS (1486.6 eV) and UPS (21.2 eV). As discussed in Section 3.4.1, in the valence band measured by XPS, YbN thin films share significant similarity in the features above 5 eV to that of Yb₂O₃ films. These features can be assigned to Yb $4f^{12}$ multiplets. On the other hand, the difference between O $2p$ orbitals in Yb₂O₃ and N $2p$ orbitals in YbN results in the features with different shapes and energy positions at around 2-5 eV.

In the UPS spectrum shown as the blue curve in Fig. 3.23, the peak centered at approximately 3.6 eV is significantly enhanced compared to that in the XPS spectrum. At around 4.7 eV, a new intense peak, which is not visible in the XPS spectrum, appears. Meanwhile,

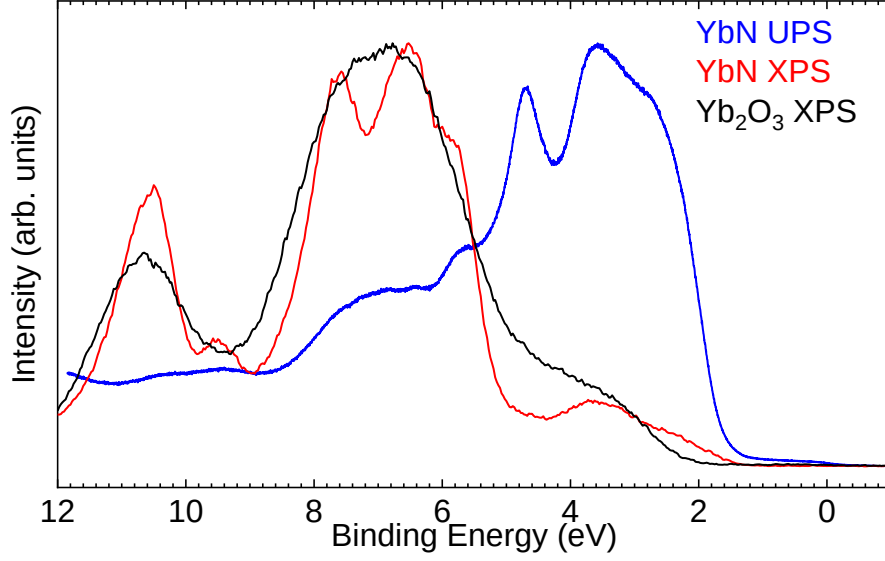


Figure 3.23: Valence band spectra measured with UPS (blue) and XPS (red) of a YbN film grown on MgO(100) at the substrate temperature of 400 °C, Yb flux rate of 8 Å/min, nitrogen plasma power of 100 W and nitrogen flow of 0.1 SCCM, together with an XPS spectrum of the Yb₂O₃ (black) as a reference. To correct for charging-induced energy shifts, the XPS spectrum of Yb₂O₃ was shifted 1.7 eV toward lower binding energy to align the Yb 4*d* core level and Yb 4*f*¹² multiplets with those of the YbN sample.

the spectral features in the region above 5 eV are significantly suppressed compared to the XPS result.

Table 3.1: Photoionization cross sections of the Yb 4*f* and N 2*p* states for the photon energies used in this study [10].

Photo energy	Yb 4 <i>f</i> (Mb)	N 2 <i>p</i> (Mb)
1486.6 (Al Kα, XPS)	8.2×10^{-2}	7.2×10^{-5}
21.2 (He-I, UPS)	1.2	9.7

To understand the aforementioned difference between the spectra measured by XPS and UPS, we consider the differences in the photoionization cross sections for the Yb 4*f* and N 2*p* states at the two photon energies used in XPS and UPS. As shown in Table 3.1, compared to the photoionization cross sections of the Yb 4*f* orbitals changing from 0.82×10^{-1} Mb for XPS and 1.2 Mb with a small enhancement factor of about 10, N 2*p* orbitals show an enhancement factor of about 10^5 with the variation of photoionization cross sections from 0.72×10^{-4} Mb to 9.7 Mb. Therefore, the features above 5 eV, whose intensity is suppressed

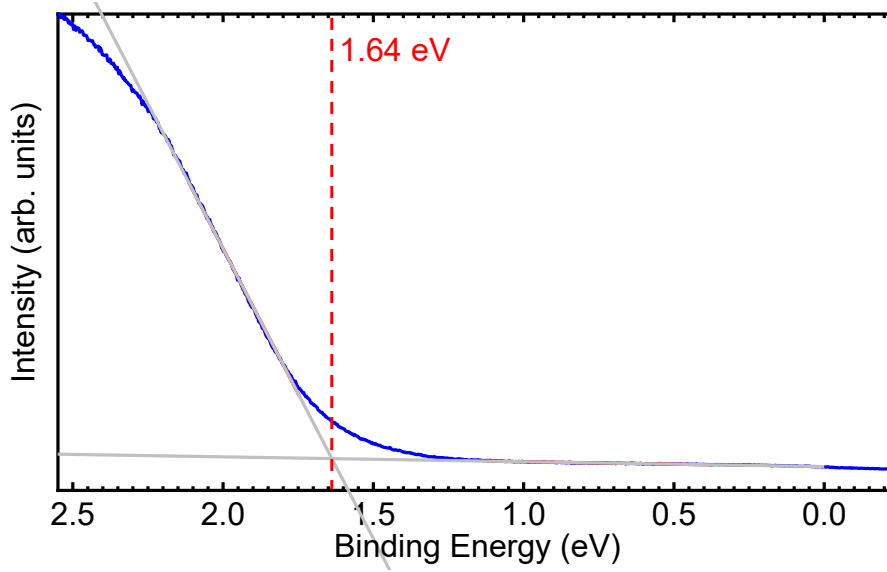


Figure 3.24: UPS spectrum that is the same as the UPS spectrum in Fig. 3.23 and zoomed up to the region near the Fermi level. Gray lines show the extrapolation of the leading edge and the background near the Fermi level of the UPS spectrum.

in UPS compared with XPS, can be identified as Yb $4f^{12}$ multiplets. On the other hand, for the peak at approximately 4.7 eV, which only appears in UPS spectrum, and the features around 3 eV, whose intensity significantly increased in UPS spectrum compared to that in XPS spectrum, can be considered to be related to the N $2p$ orbitals.

Meanwhile, one should also notice that although in the XPS spectra of YbN thin film, the features assigned to the N $2p$ orbitals are weaker than Yb $4f$ multiplets, their intensities are in the same order, despite the negligible cross section of N $2p$ orbitals compared with Yb $4f$ orbitals in this photon energy. The clearly observed N $2p$ orbitals in the XPS spectra indicate a significant p - f hybridization of the Yb $4f$ and N $2p$ orbitals in YbN thin films. This result is similar to the experimental results on epitaxially grown SmN thin films [40].

The UPS spectrum of YbN also clearly indicates a semiconducting nature of YbN. As shown in Fig. 3.24, by linear extrapolation of the leading edge of the UPS spectrum, the valence band maximum of the YbN thin film was determined to be at 1.64 eV. This value defines the lower limit of the band gap of YbN, and is in fine agreement with the previously reported YbN's optical band gap for 1.5-2 eV [71, 72]. Therefore, the presence of the band gap and thus the semiconducting nature of YbN is confirmed.

One might also notice that some residual intensity appears near the Fermi level, which

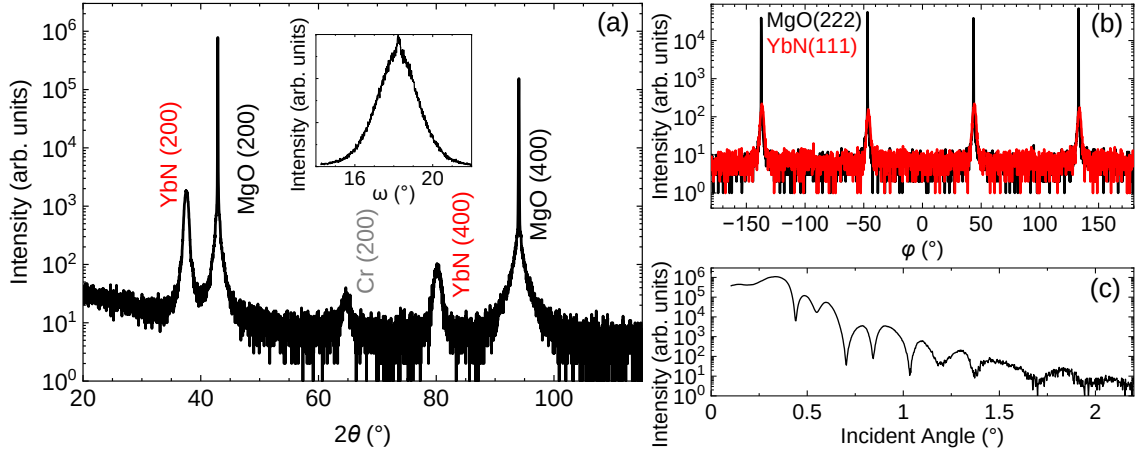


Figure 3.25: XRD of a YbN thin film grown on MgO(100) substrate at the substrate temperature of 300 °C, Yb flux rate of 5 Å/min, plasma power of 100 W, and nitrogen flow of 0.1 SCCM, capped *in situ* with about 10 nm of Cr metal, investigated by XRD measurements. (a) XRD ω - 2θ scan. The inset shows the rocking curve of the YbN (200) reflection. (b) In-plane ϕ scan of YbN(111) and MgO(222) reflections. (c) X-ray reflectivity (XRR) curve.

could be attributed to defect-induced Yb 5*d* states, similar to the defect states that were observed in the SmN epitaxial thin film [40].

3.4.3 Detailed crystal structure of YbN thin films

Finally, an *ex situ* XRD measurement was conducted for two of the epitaxial YbN thin film samples, one grown on MgO(100) and another grown on LaAlO₃(100) substrates, to obtain more information about the crystallinity of the YbN films. Before removal from the UHV system, the thin-film samples were capped with a 10-nm chromium layer to prevent degradation in air.

Figure 3.25 (a) presents the XRD ω - 2θ scan of a Cr-capped epitaxial YbN film grown on MgO(100) substrate. Peaks corresponding to MgO($2n00$) reflections from the substrates, together with YbN($2n00$) reflections, can be recognized. An additional minor peak is found near 65°, which can be attributed to the (200) reflection of Cr metal from the capping layer. The feature near 65° was also observed in the XRD ω - 2θ scan of Cr-capped SmN thin films [40], and other Cr-capped thin films, confirming that it originates from the Cr(200) reflection. Besides the peaks mentioned above, no other features could be detected in the ω - 2θ scan, indicating a well-defined (100) out-of-plane orientation of the YbN film.

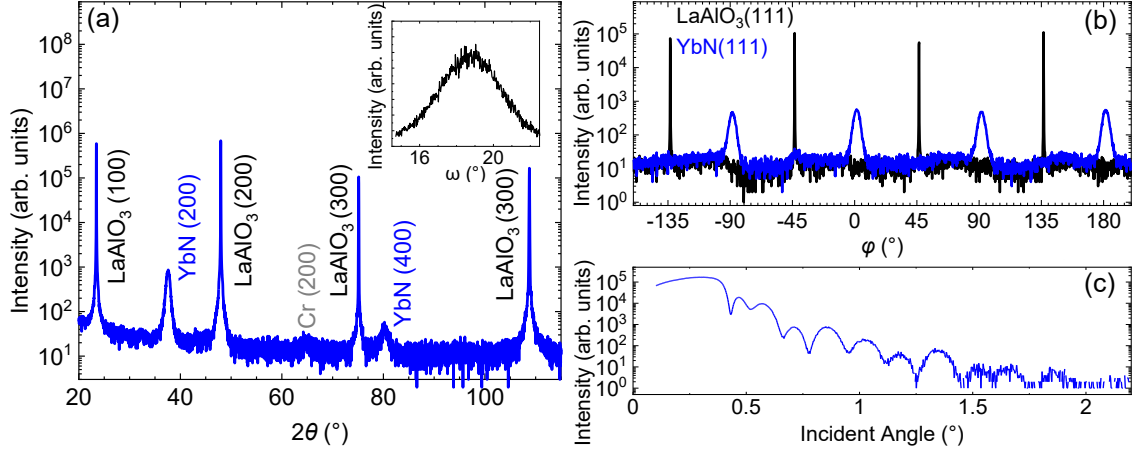


Figure 3.26: XRD of a YbN thin film grown on $\text{LaAlO}_3(100)$ substrate at the substrate temperature of 350°C , Yb flux rate of $3 \text{ \AA}/\text{min}$, plasma power of 100 W , and nitrogen flow of 0.1 SCCM , capped *in situ* with about 10 nm of Cr metal, investigated by XRD measurements. (a) XRD ω - 2θ scan. The inset shows the rocking curve of the YbN (200) reflection. (b) In-plane ϕ scan of YbN(111) and $\text{LaAlO}_3(111)$ reflections. (c) X-ray reflectivity (XRR) curve.

From the peak position of the YbN(200) and YbN(400) reflections, the lattice parameter of the YbN films was derived to be $4.786 \pm 0.008 \text{ \AA}$, which is in good agreement with the RHEED-derived value discussed in 3.3.1 as well as the reported bulk value of $4.7852 \text{ \AA}$ [68].

The rocking curve of the YbN(200) diffraction peak is shown in the inset of Fig. 3.25. The full width at half maximum (FWHM) of the rocking curve is estimated to be 2.1° . This value is similar to those of other epitaxial *REN* thin films grown by MBE with molecular nitrogen, suggesting that the YbN films grown with radical nitrogen from an RF plasma source show a similar fine crystalline quality.

Fig. 3.25 (b) exhibits the in-plane ϕ scan of the YbN(100) reflections (red) and $\text{MgO}(222)$ reflections (black). YbN(111) peaks show a fourfold symmetry and are aligned with $\text{MgO}(222)$ reflections, confirming the epitaxial growth of YbN(100) layers on $\text{MgO}(100)$ substrate without in-plane rotation.

Fig. 3.25 (c) exhibits the x-ray reflectivity (XRR) result of the YbN film grown on $\text{MgO}(100)$ surface, from which the film thickness is determined to be approximately 13.5 nm , indicating a moderate YbN growth rate of about $2.8 \text{ \AA}/\text{min}$ that is possible for the growth of high-quality thin-film samples.

Figure 3.26 shows the XRD results of a Cr-capped epitaxial YbN film grown on $\text{LaAlO}_3(100)$ surface. Similar to the result of the epitaxial YbN thin film grown on YbN, in the ω - 2θ

scan shown in Fig. 3.26 (a), only the peaks attributed to the YbN($2n00$), LaAlO₃($n00$), and Cr(200) reflections from the thin-film sample, substrate, and capping layer could be detected, indicating a (100) out-of-plane orientation of the YbN epitaxial layers grown on LaAlO₃ surface. From the ω - 2θ scan, the lattice parameter is calculated to be 4.783 ± 0.013 Å, well consistent with the value of the YbN film grown on MgO(100). Meanwhile, the FWHM of the rocking curve of the YbN (200) reflection, as shown in the inset of 3.26 (a), was estimated to be 3.6° , which is broader than that of the YbN thin film grown on MgO(100) substrate, suggesting a slightly lower crystalline quality.

Figure 3.26 (b) displays the in-plane ϕ scan of the YbN(111) reflections (blue) and LaAlO₃(111) reflections (black). a series of fourfold YbN(111) peaks appear at 45° relative to the LaAlO₃ reflections, revealing a 45° in-plane rotated growth of YbN layers on LaAlO₃(100) surface. This is in agreement with our expectation based on the lattice parameter, and also the previous reports on *REN* thin films on LaAlO₃ substrates [40, 43].

In addition, from the XRR curve shown in Fig. 3.26 (c), the film thickness and the corresponding growth rate of the YbN layer are estimated to be 15.5 nm and 1.9 Å/min.

The XRD results further confirm that the epitaxial YbN thin films with well-defined (100) out-of-plane orientation are successfully synthesized on MgO(100) and LaAlO₃(100) substrates, and that unlike other reported *REN* thin films, the YbN thin films grown on LaAlO₃(100) substrates show no apparent improvement in crystalline quality compared to the growth on MgO(100) substrates, which supports the discussion in 3.3.5.

3.5 Summary

In summary, we have successfully fabricated a (100)-oriented YbN epitaxial thin film on both MgO(100) and LaAlO₃(100) substrates, and we have investigated its crystalline and electronic structure using RHEED, XRD, XPS, and UPS. The Yb ions in the YbN thin film were found to be uniformly trivalent. Meanwhile, the VBM of YbN was determined to be at ~ 1.64 eV, suggesting the semiconducting nature. In addition, evidence of significant hybridization between the Yb 4*f* and N 2*p* states was observed.

Chapter 4

Growth Study and electronic structure of Yb-Sb thin films

In this chapter, we report the results of our growth study of Yb-Sb thin film systems. By a systematic growth study, epitaxial films of trivalent $\text{YbSb}_2(010)$ and mixed (110)- and (001)-oriented $\text{Yb}_{11}\text{Sb}_{10}$ were successfully fabricated on $\text{MgO}(100)$ substrate. In contrast, no evidence of the formation of the trivalent YbSb compound was observed. XPS further confirmed the different valence states of Sb ions in different Yb-Sb phases.

Meanwhile, we also report the growth of a YbSb_2 thin film on $\text{GaSb}(001)$ and $\text{GaSb}(110)$ substrates, along with the electronic structure observed by ARPES.

4.1 Growth study of Yb-Sb thin films on $\text{MgO}(100)$ substrates

The MBE growth and the characterization of the Yb-Sb thin films on $\text{MgO}(100)$ were done at MPI CPfS under the same conditions as mentioned in Section 3.1.2.

High-purity Sb metal was evaporated from another Knudsen effusion cell, similar to that used for Yb. During the growth, the evaporation rate of Sb (ϕ_{Sb}) was varied from 1.1 Å/min to 2 Å/min, and the evaporation rate for Yb (ϕ_{Yb}) was varied from 0.7 Å/min to 1.64 Å/min. This allowed us to adjust the evaporation rate ratio between Yb and Sb from 0.7 to 4.4 during growth. During the growth, the total deposition amount of Yb was fixed to be 25 nm.

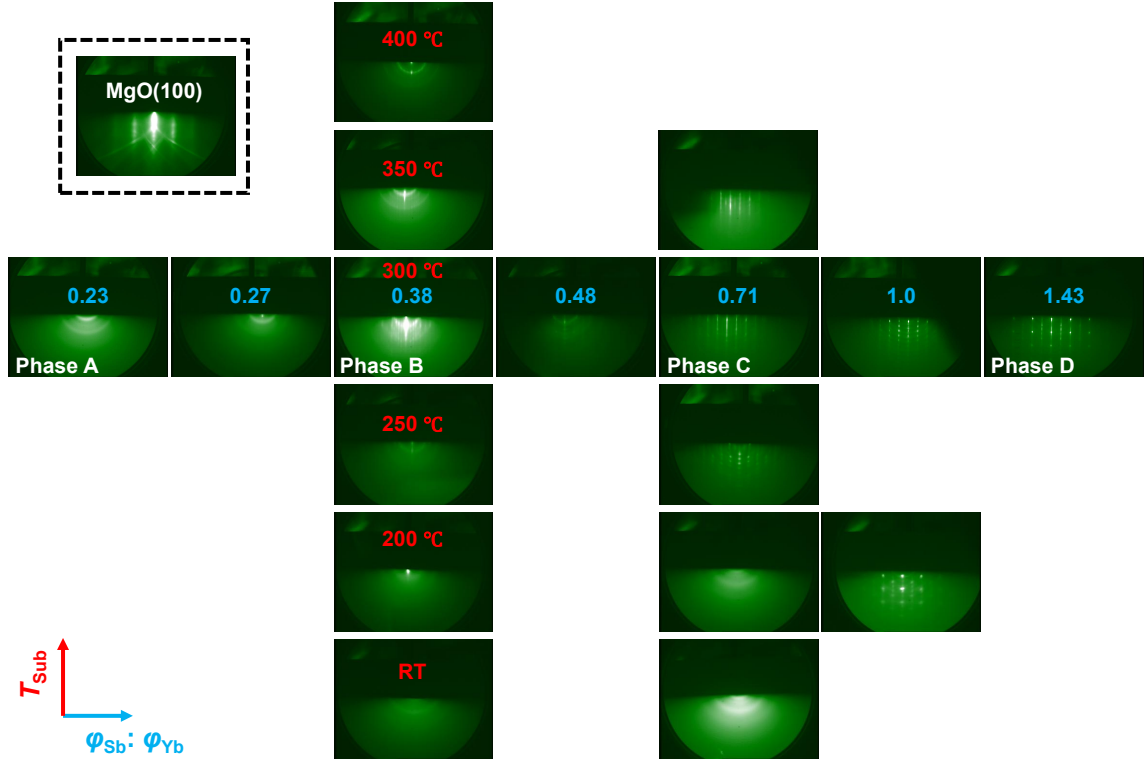


Figure 4.1: RHEED patterns of Yb-Sb thin films grown under different T_{sub} and $\phi_{\text{Sb}} : \phi_{\text{Yb}}$ after growth, together with a RHEED pattern of MgO(100) substrate before deposition.

Fig. 4.1 illustrates the RHEED pattern of Yb-Sb thin films fabricated under different T_{sub} and $\phi_{\text{Sb}}/\phi_{\text{Yb}}$. As shown in Fig. 4.1, when the substrate temperature is low (< 200 °C), only ring-like structures can be observed in RHEED patterns. This suggests a randomly oriented surface, possibly because the temperature is not hot enough for the reaction between deposited Yb and Sb atoms, or for forming an ordered structure.

When the substrate temperature exceeds 250 °C, different features begin to appear. With the increasing $\phi_{\text{Sb}}/\phi_{\text{Yb}}$, four kinds of typical RHEED patterns were observed, which are named as Phases A-D. The enlarged version of the RHEED patterns of Phases A-D is shown in Fig. 4.2. When the $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ is low (Phase A), only ring-like structures are ex-

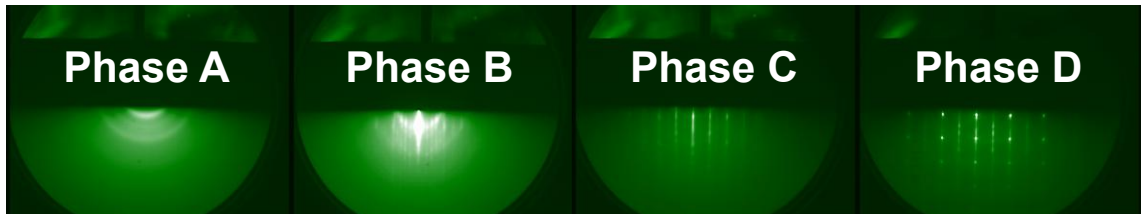


Figure 4.2: Enlarged RHEED patterns of Phases A-D.

hibited, suggesting a polycrystalline surface. When the $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ increases to approximately 0.38 (Phase B), streaks appear in the RHEED pattern, suggesting the epitaxial growth. The RHEED pattern is easily recognizable, with a strong central streak and numerous weaker streaks around it, suggesting a much larger lattice parameter than that of the MgO(100) substrate and/or a long-range surface reconstruction. However, the detailed lattice parameter cannot be determined solely from the RHEED pattern, since the composition and structure are unknown.

When $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ becomes even larger, around 0.7-1 (Phase C), a different RHEED pattern: double-periodic streaks (with faint quadra-periodic streaks) regarding that of MgO(100), appears, indicating the formation of a different compound compared with Phase B. By comparing the spacing between the RHEED pattern of the film and the MgO substrate, the lattice parameter is estimated to be about $4.2 \pm 0.1 \text{ \AA}$.

When $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ further increases into the Sb excessive region (Phase D), the RHEED pattern changes again. Although the spacing of the streaks is similar to Phase C, the appearance of the streaks, or in other words, the intensity relation between different streaks or transmission spots, is different.

To understand the exact composition of the different phases, the detailed crystalline structure of the fabricated films was investigated by *ex situ* XRD measurement after capping with 10-nm Cr layers. As indicated by the RHEED pattern, Phase A is completely in a randomly oriented polycrystalline phase, and therefore, no signal except for the peaks of the substrates could be observed by XRD ω - 2θ scan, and the XRD result is therefore omitted here.

The XRD ω - 2θ scan of Phase B ($\phi_{\text{Sb}}/\phi_{\text{Yb}} = 0.38$, $T_{\text{sub}} = 300 \text{ }^\circ\text{C}$) is shown by the blue curve in Fig. 4.3. Besides the sharp (200) and (400) reflection peaks of the MgO substrate, there are two sets of well-defined peaks marked by gray and black, while no other peaks could be observed. These two series are determined to be the $(nn0)$ reflections (gray) and $(002n)$ reflections of $\text{Yb}_{11}\text{Sb}_{10}$. From the peak positions of the two series of reflection peaks, the lattice parameters of the fabricated $\text{Yb}_{11}\text{Sb}_{10}$ film are derived to be $c = 17.24 \pm 0.02 \text{ \AA}$, $a = b = 11.93 \pm 0.02 \text{ \AA}$. These values are reasonably consistent with the reported bulk lattice parameters of $\text{Yb}_{11}\text{Sb}_{10}$ ($a = b = 11.86 \text{ \AA}$, $c = 17.10 \text{ \AA}$ [91]). This result, together with the RHEED pattern, suggests that the sample is an epitaxial $\text{Yb}_{11}\text{Sb}_{10}$ thin film with mixed (110) and (001) orientation.

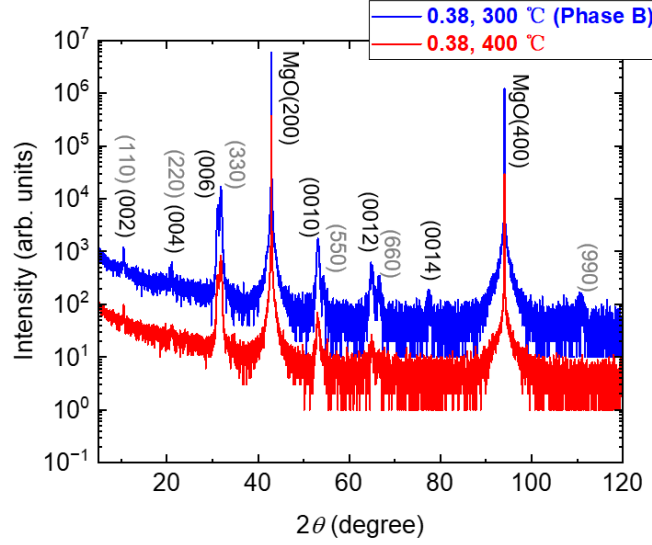


Figure 4.3: XRD of Phase B (blue, $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 0.38$, $T_{\text{sub}} = 300$ °C) and the film grown at the same conditions of Phase B, except for a substrate temperature of 400 °C. The blue curve is shifted upwards for clarity.

For the film grown at $T_{\text{sub}} = 400$ °C, the same peaks, but weaker than those of Phase B, are observed, indicating that it has the same composition but worse crystal quality. This result is consistent with the observed degraded RHEED pattern at high substrate temperature shown in Fig. 4.1.

We now further consider whether it is reasonable for $\text{Yb}_{11}\text{Sb}_{10}$ grown on $\text{MgO}(100)$ surface from a point of view of lattice mismatch. For $\text{Yb}_{11}\text{Sb}_{10}(001)$ layers, lattice parameter is 11.86 Å. Given the lattice parameter of $\text{MgO}(100)$ of 4.21 Å, when a in-plane 45 °-rotated growth is considered, the effective lattice parameter of the substrate can be $4.21 \times 2\sqrt{2} = 11.9$ Å, with only 0.3 % lattice mismatch with $\text{Yb}_{11}\text{Sb}_{10}(001)$. Similarly, for $\text{Yb}_{11}\text{Sb}_{10}(001)$ layers, the lattice parameters are 16.77 Å and 17.10 Å, which both match well with four times the lattice parameter of $\text{MgO}(100)$ of 16.8 Å, with lattice mismatches of only 0.4 % and -1.5 %, respectively. These well-matched values support the result of the epitaxial growth of $\text{Yb}_{11}\text{Sb}_{10}$ layers in a mixture of (110) and (001) orientation.

The films grown under conditions around phases C and D are shown in Fig. 4.4. While Phase C ($\phi_{\text{Sb}}/\phi_{\text{Yb}} = 0.71$, $T_{\text{sub}} = 300$ °C) shown in black only exhibits $\text{YbSb}_2(060)$ reflection peaks besides the $\text{MgO}(200)$ and $\text{MgO}(400)$ reflections from the substrate, other three curves show the well identified whole series of $(02n0)$ reflection peaks of YbSb_2 . From the peak positions of YbSb_2 reflections, the lattice parameters are derived to be 16.72 ± 0.02 Å,

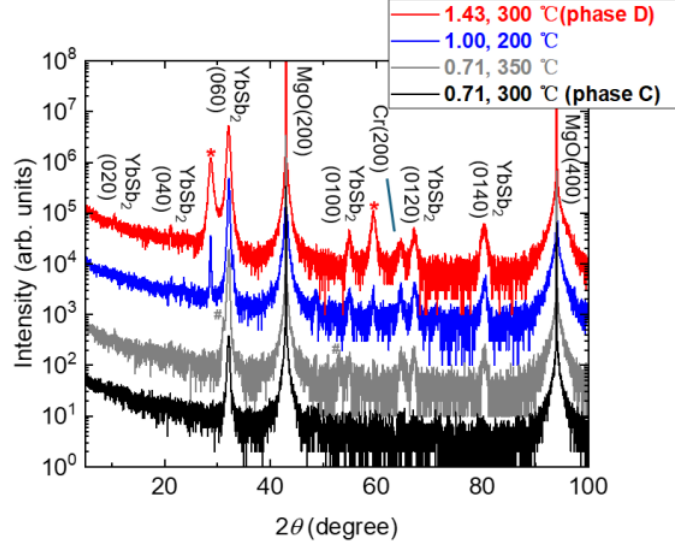


Figure 4.4: XRD of Phase C (black, $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 0.71$, $T_{\text{sub}} = 300$ °C), the film grown at the same conditions as Phase C, except for the substrate temperature of 350 °C (gray), the film grown at $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 1.00$, $T_{\text{sub}} = 200$ °C (red), and Phase D (blue, $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 1.43$, $T_{\text{sub}} = 300$ °C). Each curve is shifted upward for clarity.

which matched perfectly with the bulk value ($b = 16.72$ Å) [80] and that of the previously reported YbSb₂(010) epitaxial thin film grown on GaSb(001) substrate [51]. This suggests that these films are mainly composed of YbSb₂(010).

At the same time, the films grow in comparatively Sb-rich phases (red and blue); another series of peaks is marked by a red asterisk. From the peak positions of these two peaks, the lattice plane distance is calculated to be 3.10 ± 0.01 Å. There are two possibilities for this series of reflections. The first is the $(2n00)$ reflections of YbSb crystallized in NaCl structure with a lattice parameter of 6.079 Å [84], while the other is the $(n00)$ reflections of Sb metal crystallized in primitive cubic α -Po structure with a lattice parameter of 3.10 Å [137]. Considering the similarity in lattice parameter and the fact that these peaks appear in films grown under Sb-richer conditions than the YbSb₂ film (Phase C), this series of peaks is attributed to the $(n00)$ reflections of Sb metal.

One might also notice that in the XRD result of the film grown at $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 0.71$, $T_{\text{sub}} = 300$ °C, as shown in gray, comparatively weak structures marked by "#" are observed. These structures correspond to the (330) and (550) reflections of YbSb₂ as shown in Fig. 4.3, indicating that this film is a mixture of YbSb₂ and Yb₁₁Sb₁₀. This fact is rather essential, as it suggests that when we try to vary the Yb: Sb ratio in MBE growth of Yb-Sb

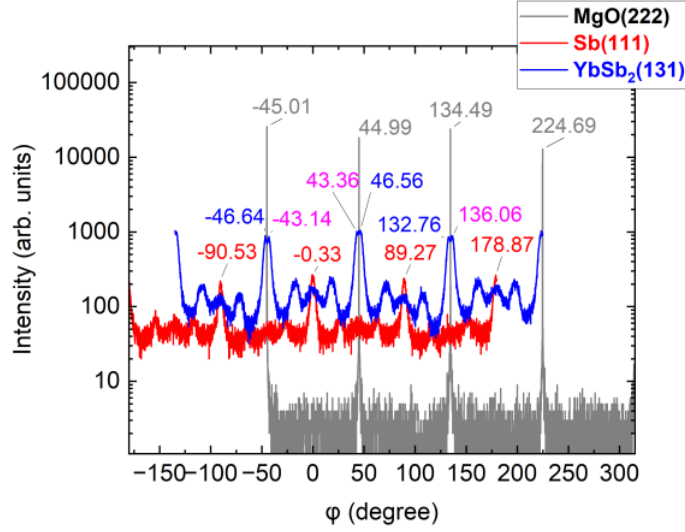


Figure 4.5: In-plane ϕ scan of MgO(222) (black), Sb(111) (red), and YbSb₂(131) reflections of the Yb-Sb thin film grown at $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 1.00$, $T_{\text{sub}} = 200$ °C.

film, it will change from Yb-rich $\text{Yb}_{11}\text{Sb}_{10}$ phase directly to Sb-rich YbSb_2 phase, or vice versa, while no 1: 1 YbSb phase is formed between them. The absence of Yb-trivalent YbSb could be considered as follows: First of all, the electron affinity of Sb is lower than that of lighter Pn elements, which makes its Yb-Sb compounds with divalent Yb ions the more stable form. In fact, a recent study on the growth of a YbSb bulk sample suggests that $\text{Yb}_{11}\text{Sb}_{10}$ is rather stable and could be the main impurity of about 4 % in even an "ideal" YbSb sample [85].

On the other hand, since the powder sample of YbSb exists[86–88], there should be other reasons in addition to the electron affinity of Sb. One possible explanation is the insufficient reactivity of the Sb_4 supplied from the K-cell.

Figure 4.5 exhibits the in-plane ϕ scan of the Yb-Sb thin film grown at $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 1.00$, $T_{\text{sub}} = 200$ °C, i.e., the same film as that shown by the red curve in Fig. 4.4, which is considered to be a mixture of $\text{YbSb}_2(010)$ and $\text{Sb}(100)$. As shown by the red curve, Sb(111) peaks show a fourfold symmetry and appear at 45° relative to the MgO(222) reflections, indicating the 45° -rotated growth of Sb(111) layers on MgO(100), which is consistent with the expectation.

For $\text{YbSb}_2(131)$ reflections, as shown by the blue curve, there are two sets of reflection peaks marked in blue and magenta, respectively. Two-fold symmetric peaks appearing

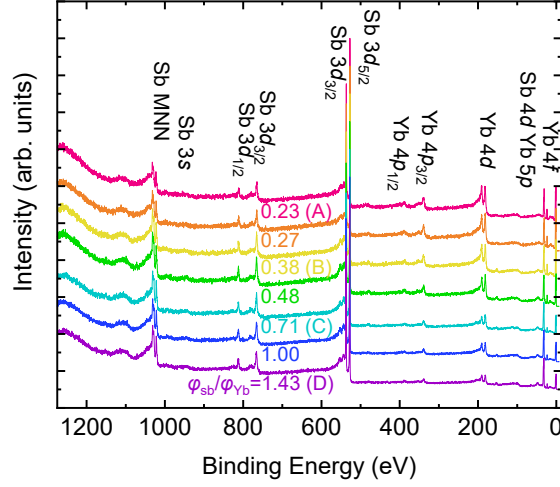


Figure 4.6: XPS wide-range spectra of Yb-Sb thin films grown on MgO(100) substrates at the substrate temperature of 300 °C and the indicated value of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$. The spectra are normalized to their highest peak. Each spectrum is shifted upwards for clarity.

near the MgO(222) reflection in a spacing of approximately 87° and 93° in each set. This spacing is consistent with the calculation based on the lattice parameter and with the previously reported result for YbSb₂(010) films grown on a GaSb(001) substrate [51], further supporting that the fabricated film is YbSb₂(010). Meanwhile, the existence of the two sets of reflection peaks suggests the existence of two domains rotated 90° in-plane compared with each other, which is different from the situation of growth on GaSb(001), where the [001] direction of YbSb₂ always aligns with the [110] direction of GaSb [51]. This can be attributed to the fact that, compared with the (001) surface with two-fold symmetry of zinc-blende structured GaSb, the (100) surface of MgO exhibits a four-fold symmetry where the [010] and [001] directions are equivalent.

From the RHEED and XPS results, phases B, C, and D are attributed to be Yb₁₁Sb₁₀(001), (phase that is very close to) YbSb₂(010), and a mixture of YbSb₂(010) and Sb(100). We now further verify this conclusion and investigate the electronic state using XPS.

Figure 4.6 exhibits the wide-range XPS spectra of Yb-Sb thin films grown under different values of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$. In general, all the spectra show a similar spectral shape, where the peaks are from only Yb and Sb, without any other impurities that could be detected. Meanwhile, one can easily notice that when the value of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ is lower than 0.48, the intensity of Yb 4p, 4d and 4f increase evidently, indicating that they are in Yb-rich phases, which

consistent with our XRD results that suggests the change between YbSb_2 phase to $\text{Yb}_{11}\text{Sb}_{10}$ phase occurs in this region.

We then look into the XPS result in each core level in more detail, as shown in Fig. 4.7. As shown in Fig. 4.7 (c) and (d), in the Yb 4*d* core level and valence band, the spectral shape of all the Yb-Sb films is consistent with that of the Yb-metal film. At the same time, no significant features corresponding to Yb^{3+} are detected. These facts indicate that Yb ions in all these films are predominantly divalent.

One might also notice that some spectra in Fig. 4.7 (e) also exhibit some structure around 5-20 eV, which are considered to originate from a small amount of Yb^{3+} ions. Meanwhile, there are also small hump-like features that appear at approximately 531 eV in those films that show trivalent contribution, as shown in the inset of Fig. 4.7 (a), indicating that the observed signal from Yb^{3+} is from the partial oxidation of the thin-film samples. The reason for the partial oxidation was further verified to be the oxidation process during the XPS measurement, as discussed in Section 3.3.6.

As $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases, the Sb 3*d* and 4*d* peaks first remain nearly unchanged until Phase C ($\phi_{\text{Sb}}/\phi_{\text{Yb}}$), as shown in Fig. 4.7 (a) and (b). When $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases towards Phase B, Sb core-level peaks become broader and shift to lower binding energies. After that, when $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases further, Sb 3*d* and 4*d* core-level peaks become sharp again and stop shifting further towards the lower binding energy side.

On the other hand, Yb core-level spectra and Yb 4*f* also change depending on the value of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$, but with different behavior and not as significantly as the changes of the Sb core-level spectrum. When $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases from 0.71 (Phase B) towards 0.38 (Phase B), the intensity of Yb core-level spectra increases, which could be easily seen by comparing the intensity of Sb 4*d* state and Yb 5*p* state in Fig. 4.7 (b). At the same time, the spectral shape of Yb 4*d*, 5*p*, and 4*f* states remains nearly unchanged, and the peaks are shifted to higher binding energy only by about 0.1 eV, which is much smaller than the energy shift of Sb core levels in this region. As $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases further towards 0.23 (Phase A), while the energy of Sb core levels saturates and their peaks become sharp again, the Yb 4*d*, 5*p*, and 4*f* states broaden and shift to higher binding energies significantly.

These unsynchronized changes of Yb and Sb states in Yb-Sb thin films, depending on $\phi_{\text{Sb}}/\phi_{\text{Yb}}$, can be understood as follows:

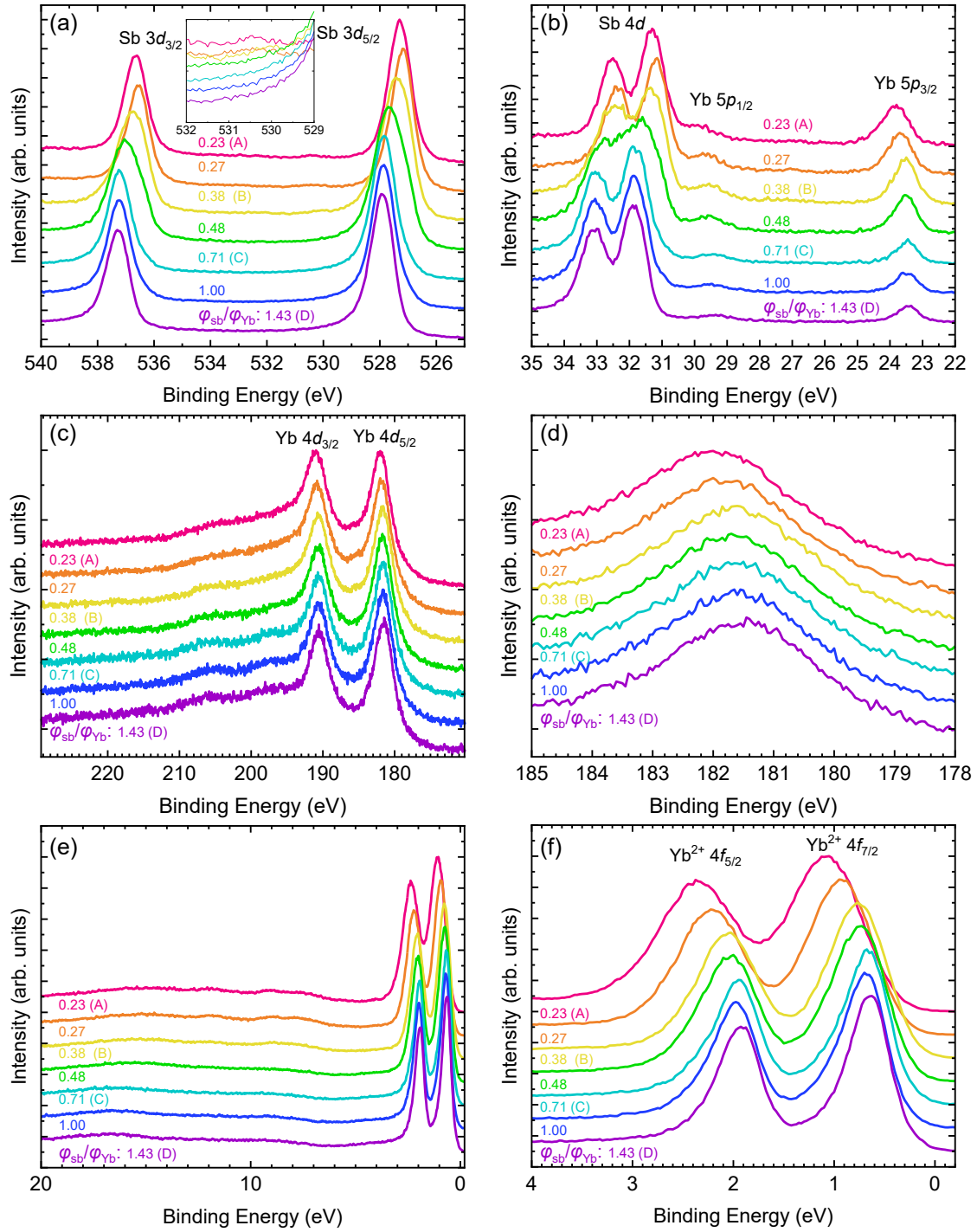


Figure 4.7: XPS spectra of Yb-Sb thin films grown on MgO(100) substrates at the substrate temperature of 300 °C and the indicated value of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$. All the spectra are normalized to their highest peak, and each spectrum is shifted upward for clarity. (a) Sb 3d core-level spectra. The inset shows the expanded spectra near the O 1s region. (b) Sb 4d and Yb 5p core-level spectra. (c) Yb 4d core-level spectra. (d) Same spectra as (c), focused on Yb 4d_{5/2} region. (e) Valence band spectra. (f) Same spectra as (e), focused on Yb²⁺ 4f region.

When $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases from 0.71 (Phase C) towards 0.38 (Phase B), the composition of the film changes from YbSb_2 to $\text{Yb}_{11}\text{Sb}_{10}$, with the increasing Yb content in the films, resulting in the intensified Yb core-level spectra compared to those of Sb. In YbSb_2 , Yb ions are divalent, and therefore the Sb ions are considered to be in the Sb^{1-} state. On the other hand, a $\text{Yb}_{11}\text{Sb}_{10}$ unit cell contains 11 of Yb^{2+} , 4 of Sb^{3-} ions, 1/2 of $[\text{Sb}_4]^{4-}$ ions and 2 of $[\text{Sb}_2]^{4-}$ [90]. Therefore, the Sb ions in $\text{Yb}_{11}\text{Sb}_{10}$ could be considered in a mixture of monovalent, divalent, and trivalent states. This explains the broadening and the energy shift to the low-binding-energy side of the Sb core-level spectra when changing from Phase C to Phase B, as the more "reduced" Sb^{2-} and Sb^{3-} ions appear in addition to Sb^{1-} ions that exist in YbSb_2 . In the meantime, the valence state of Yb remains unchanged, while its chemical environment becomes slightly more oxidizing. This results in a minor energy shift toward higher binding energies for Yb states.

The again sharpened Sb core-level spectra and the saturated energy shift to the lower binding energy side as further decreases of $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ towards Phase D indicate the disappearance of Sb^{1-} states while Sb^{3-} and possibly also Sb^{2-} states remain. This suggests the formation of Yb-rich phases such as Yb_4Sb_3 or Yb_5Sb_3 . This is further convinced by the fact that Yb core-levels and Yb 4*f* states shift to high binding energies, suggesting a more "oxidized" state of Yb ions, although they are still divalent. Meanwhile, the broadening of the Yb core-level and valence band spectra suggests the multiple types of chemical environment for Yb ions, indicating that Phase D could be a mixture of Yb-Sb compounds (and Yb metal). The detailed chemical compensation in Phase D, and whether epitaxial thin-film samples of Yb-rich compounds can be fabricated at higher substrate temperatures or lower $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ ratios, remain to be investigated in further studies.

One might also notice that when $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ decreases from 1.43 (Phase D, mixture of YbSb_2 and Yb metal) to 0.71 (Phase C, YbSb_2), the Sb core-level spectra remain nearly unchanged. This might be because the difference in the energy position of core levels of Sb^0 and Sb^{1-} is much smaller than the spectral width. For example, for the Yb 3*d*_{5/2} peak, the energy difference was calculated to be approximately 0.3 eV using the energy position of the Yb metal reference film and the reported value for Yb metal [138], while the spectral width (FWHM) of the spectrum of YbSb_2 is estimated to be about 1.1 eV.

Figure 4.8 shows the Yb 3*d*/Sb 4*d* ratios of Yb-Sb thin films grown at $T_{\text{sub}} = 300$ °C. The values were derived from the integrated intensities of the corresponding spectra and

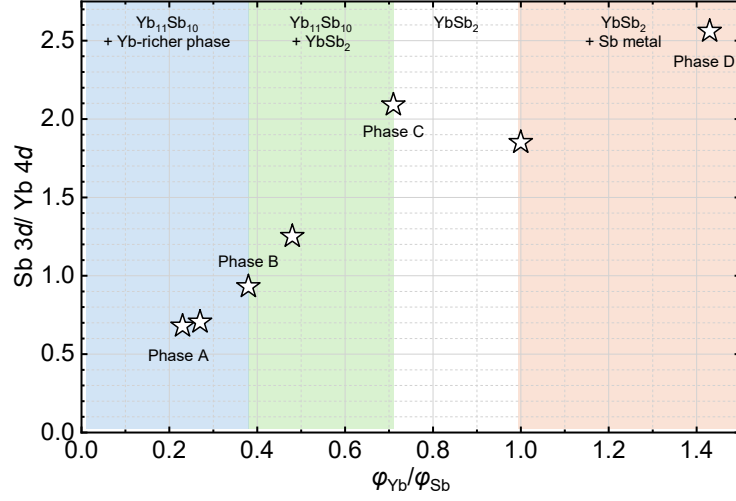


Figure 4.8: ϕ_{Sb}/ϕ_{Yb} dependence of Sb 3d/Yb 4d ratios calculated from the integrated intensities of the corresponding XPS spectra shown in Fig. 4.7.

corrected by photoionization cross sections from Ref. [10]. This result further confirmed the conclusions from the chemical compositions obtained from the XRD and XPS measurements: Phase B and C are Yb₁₁Sb₁₀ and YbSb₂, with Yb/Sb ratios slightly smaller than 1 and approximately 2, respectively, while Phase A and D are in Sb-rich phase and Yb-rich phase (mixture of YbSb₂ and Yb metal), with Yb/Sb ratios of about 0.7 and 2.5, respectively.

4.2 Growth and electronic structure of YbSb₂ thin films on GaSb

In order to investigate the electronic structure of YbSb₂ epitaxial thin films, the growth of the YbSb₂ thin film, the characterization of the surface atomic structure by LEED, and the synchrotron-based APRES measurement were conducted *in situ* at BL7U, UVSOR-III in Okazaki, Japan.

The growth was conducted in the preparation chamber, with a base pressure better than 1×10^{-7} Pa. High-purity Yb and Sb metals were evaporated from hand-made K-cells as shown in Fig. 2.3, which were prepared in the laboratory at The University of Osaka, and installed into the preparation chamber at the beamline before the beam time. A quartz crystal thickness monitor was also installed to measure the flux rate of Yb and Sb

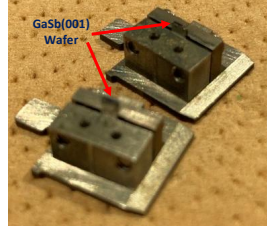


Figure 4.9: A photo of the sample holders for preparing GaSb(110) substrates by cleaving *in situ*.

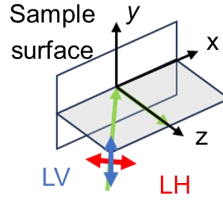


Figure 4.10: A schematic illustration of the geometry of ARPES measurement at BL7U, UVSOR-III.

evaporators at the growth position. During the growth, the flux rates of Yb and Sb were set to satisfy $\phi_{\text{Sb}}/\phi_{\text{Yb}} = 1.0 \pm 0.1$, with the flux rate of each evaporator being about 1 Å/min. The deposition time was adjusted for each growth to make the total deposition amount of Yb approximately 1.5 nm.

GaSb(001) and GaSb(110) substrates are used for the growth of YbSb₂ thin films in this study. GaSb(001) and GaSb(110) epi-polished wafers were cleaned by Ar-ion sputtering in the UHV system at $T_{\text{sub}} = 450$ °C for about 30 min. Meanwhile, GaSb(110) substrates were also prepared by cleaving GaSb(001) wafers along the (110) plane *in situ* using a specially designed sample holder, as shown in Fig. 4.9. During growth, the temperature of the GaSb substrates was maintained at 300 °C, monitored in real time with a pyrometer.

After growth, the surface atomic structure of the thin-film samples was measured *in situ* with LEED, and then the electronic structure was investigated using synchrotron ARPES at around 10 K. For ARPES measurement, both horizontally linear-polarized (LH) and vertically linear-polarized (LV) 21-eV photons were used. LH and LV correspond to *p*- and *s*-polarized light, respectively, as introduced in Section 2.2.3. The energy resolution was estimated to be approximately 20 meV. The sample temperature was fixed at approximately 10 K. The geometry of the ARPES measurement is shown in Fig. 4.10.

Before the growth of YbSb₂ epitaxial film on GaSb(001) substrate, the clean GaSb(001) surface with $c(2 \times 6)$ surface reconstruction, whose LEED pattern is shown on the left of

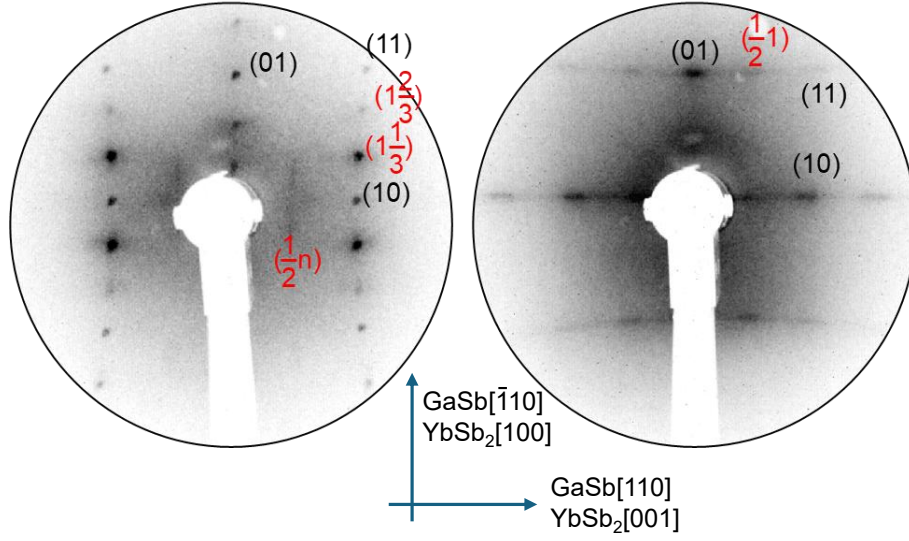


Figure 4.11: LEED patterns of GaSb(001)-c(6 $\times$ 2) clean surface (left) and YbSb₂(2 $\times$ 1) reconstructed surface after growth (right), measured using 79-eV electrons.

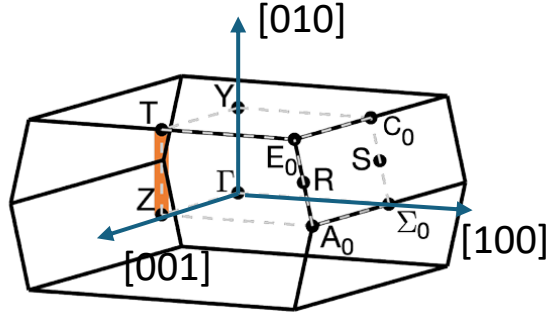


Figure 4.12: The bulk Brillouin zone of YbSb₂.

Fig. 4.11, was prepared by Ar-ion sputtering and annealing under the conditions mentioned previously. After growth, the LEED pattern changed to a (2 $\times$ 1) reconstructed surface whose LEED pattern is shown on the right of Fig. 4.11. This is consistent with the reported growth of epitaxial YbSb₂(010) layers on GaSb(100) substrate introduced in Fig. 1.15 in Section 1.1.4 [51], indicating the successful growth of YbSb₂(010) epitaxial thin film, with YbSb₂[001] direction aligned to GaSb[110] direction.

The bulk Brillouin zone of YbSb₂ is illustrated in Fig. 4.12. Since the 21-eV VUV photons were used, the uncertainty of out-of-plane momentum k_z is about 0.2 Å⁻¹. Given the out-of-plane lattice parameter $b = 16.72$ Å of (010)-oriented YbSb₂ thin film, the magnitude of the size of the Brillouin zone along the out-of-plane [010] direction is estimated to be

about $0.4 \text{ \AA}^{-1}$, which is comparable to the intrinsic k_z broadening. Therefore, the observed band dispersions should be considered as an averaged dispersion along the whole Brillouin zone on the $[010]$ direction. i.e., the observed band dispersion along the $[100]$ direction is expected to be an average of the Γ - Σ_0 like dispersions and Y- C_0 like dispersions, while the dispersion along the $[001]$ dispersion is expected to be an average of dispersions along the Γ -Z line and that along the Y-T line.

The ARPES intensity maps together with the corresponding curvature plots along $[001]$ and $[100]$ directions of YbSb_2 are shown in Fig. 4.13 and 4.14, respectively. Significantly different band dispersions are observed along the two directions, which could be attributed to the two-fold rotational symmetry of $\text{YbSb}_2(010)$ surface together with the (2×1) surface reconstruction. The flat band located at around 0.6-0.8 eV is attributed to the $\text{Yb}^{2+} 4f_{7/2}$ state, whose energy position consistent with that of XPS result of the $\text{YbSb}_2(010)$ thin film grown on $\text{MgO}(100)$ (Fig. 4.7 (e) and (f)), and that of reported calculation result (Fig. 1.14 (b)) or ARPES result (Fig. 4.15) [53]. Meanwhile, compared with the previously reported ARPES of bulk YbSb_2 in which only a broad hole-like shadow near the Γ point could be observed, the ARPES results in the present study exhibit clearer dispersions.

We then look into the ARPES results in more detail. For the ARPES results along the $[001]$ direction as shown in Fig. 4.13, the dispersions with a minimum at around 0.6 eV and a top at around 0.8 eV near the $\Gamma(\text{Y})$ point, and the structures symmetric with respect to the Z(T) point observed by LH photons are qualitatively consistent to the calculated band dispersions along the Γ -Z line and the Y-T line as shown in Fig. 4.13 (e) and (f).

One would notice that the structures that share fair similarities to those observed near the Z(T) point by the LH photons, also appear near the $\Gamma(\text{Y})$ point in the ARPES intensity map measured by the LV photons, as shown in the area surrounded by the red squares. Also, in the region surrounded by the white square measured in the ARPES results measured by LH photons, dispersions seem to be symmetric with respect to the middle point of the $\Gamma(\text{Y})$ -Z(T) line.

Figures 4.13 (g) and (f) show the calculated band dispersions (solid lines) together with a replica (dashed line) of the calculated band dispersions, assuming a double-period band folding, overlaid onto the curvature plots exhibited in Fig. (c) and (d). The qualitative similarity of the dispersions near the Γ and X point between calculation and ARPES result can be more easily seen, and the complex dispersions that are symmetric with respect to

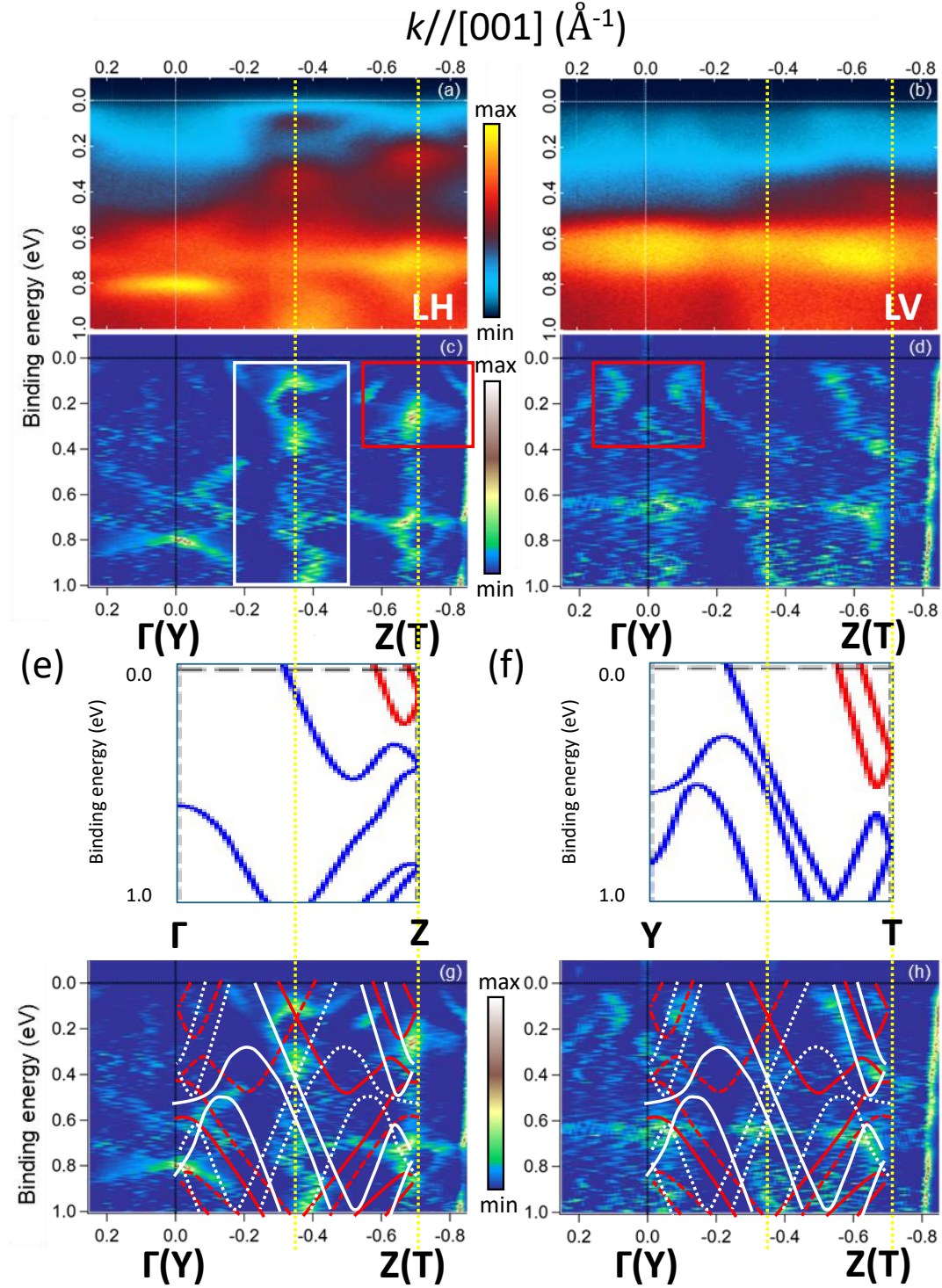


Figure 4.13: ARPES intensity plot measured along $\text{YbSb}_2[001]$ direction (parallel to Z- Γ -Z line of the bulk Brillouin zone) with (a) LH 21-eV photons and (b) LV 21-eV photons. (c) The curvature plot corresponds to (a). (d) The curvature plot corresponds to (b). (e-f) Calculated band dispersions along Γ -Z and Y-T line extracted from Ref. [54]. (g-h) Calculated band dispersion along Γ -Z direction (red) and Y-T direction (white) plotted on top of the curvature plots shown in (c) and (d). Solid lines exhibit the calculated band dispersions while dashed lines show the replica bands corresponding to a double period super period on the $[001]$ direction due to the observed ($2\times$) surface reconstruction.

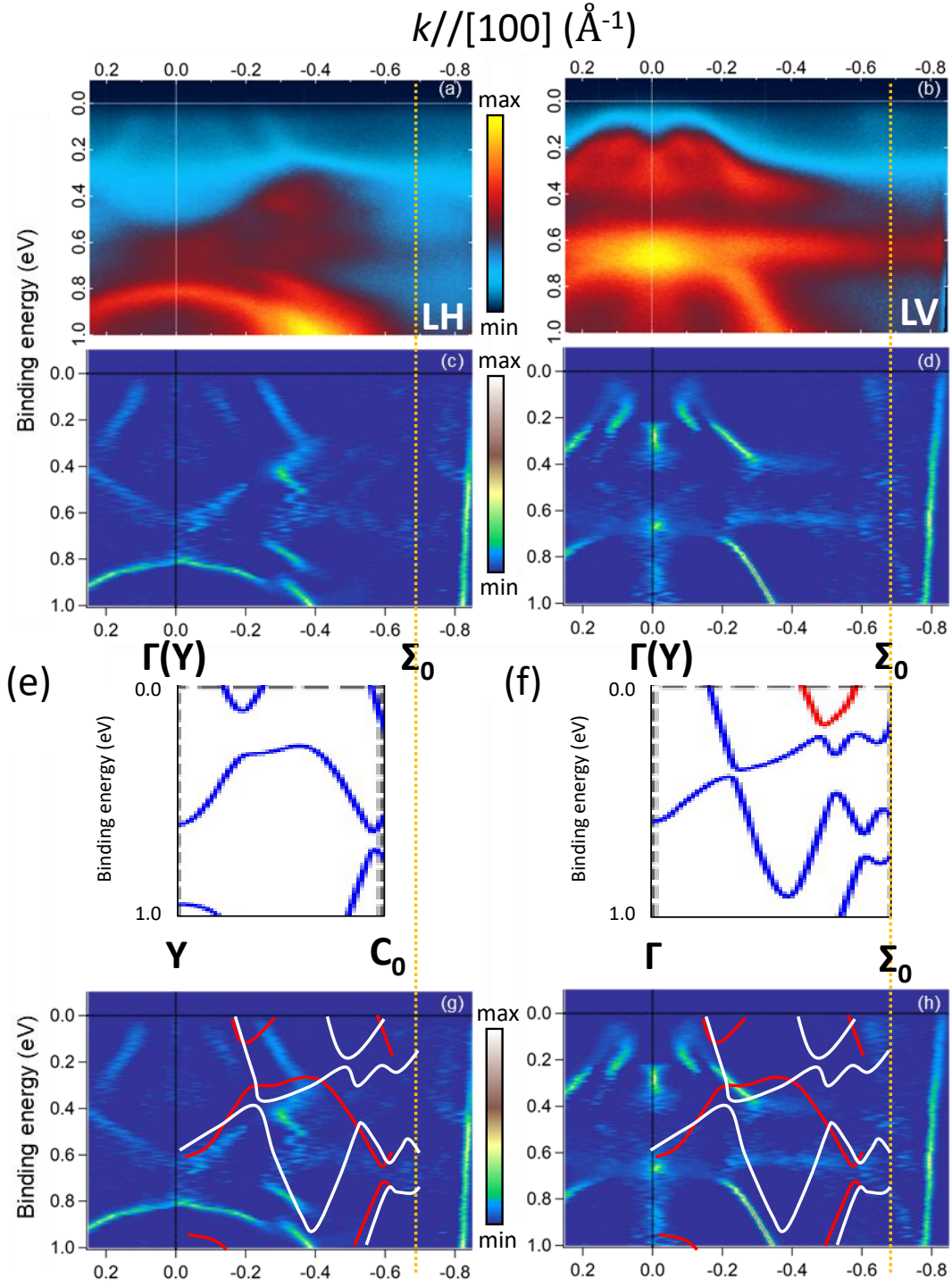


Figure 4.14: ARPES intensity plot measured along $\text{YbSb}_2[100]$ direction (parallel to Σ_0 - Γ - Σ_0 line of the bulk Brillouin zone with (a) LH 21-eV photons and (b) LV 21-eV photons. (c) The curvature plot corresponds to (a). (d) The curvature plot corresponds to (b). (e-f) calculated band dispersions along Γ - Σ_0 and Y - C_0 line extracted from Ref. [54]. (g-h) Calculated band dispersion along Γ - Σ_0 (red) and Y - C_0 direction (white) plotted on top of the curvature plots shown in (c) and (d).

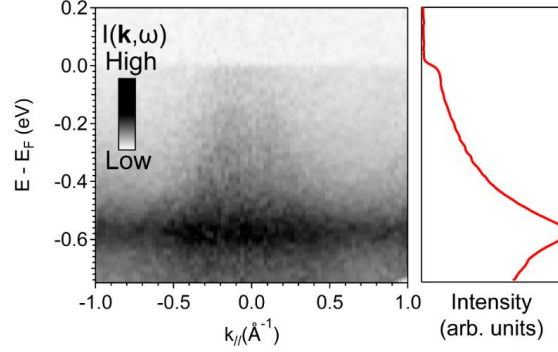


Figure 4.15: AREPS and the corresponding angle-integrated spectra of bulk YbSb_2 [53].

the middle point of Γ -Z can be explained by the crossing of the original and replica bands.

On the other hand, for the ARPES results along the $[100]$ direction as shown in Fig. 4.14, the dispersions with a bottom at around 0.6 eV and a top at around 0.8 eV near the $\Gamma(\text{Y})$ point, as well as the linear-like dispersions across the Fermi energy at around $0.1 \text{ \AA}^{-1}$ and $0.2 \text{ \AA}^{-1}$ are also qualitatively consistent with the calculation result. Meanwhile, no evidence of complex dispersions or band folding appearing in the ARPES result along the $[001]$ direction could be observed along the $[100]$ direction. This indicates that the ARPES-observed dispersion of the $\text{YbSb}_2(010)$ epitaxial thin film is qualitatively consistent with the observed surface crystal structure with (2×1) reconstruction.

The LEED pattern of $\text{GaSb}(110)$ clean surface is exhibited in Fig. 4.16 (a), in which rectangular diffraction spots are observed, suggesting a (1×1) surface without reconstruction. $\text{GaSb}(110)$ substrate prepared by Ar-ion sputtering and annealing exhibits the same LEED pattern as 4.16 (a), which is omitted here.

For the growth on substrates prepared by both cleaving and Ar-ion sputtering and annealing, after deposition of Yb and Sb, identical LEED patterns with streak-like structure extending in the $[001]$ direction of $\text{GaSb}(110)$ substrates are observed, as shown in Fig. 4.16 (b) and (c). This indicates the identical growth results on both substrates, with a one-dimensional-like growth along $[\bar{1}10]$ direction of $\text{GaSb}(110)$ substrate, while the long-range periodicity along $[001]$ direction of $\text{GaSb}(110)$ surface is missing.

One might notice that the diffraction spots and streaks appear on a set of curved lines. The cause is geometric projection distortion when a two-dimensional flat sensor in a camera captures the LEED pattern on a three-dimensional spherical LEED screen.

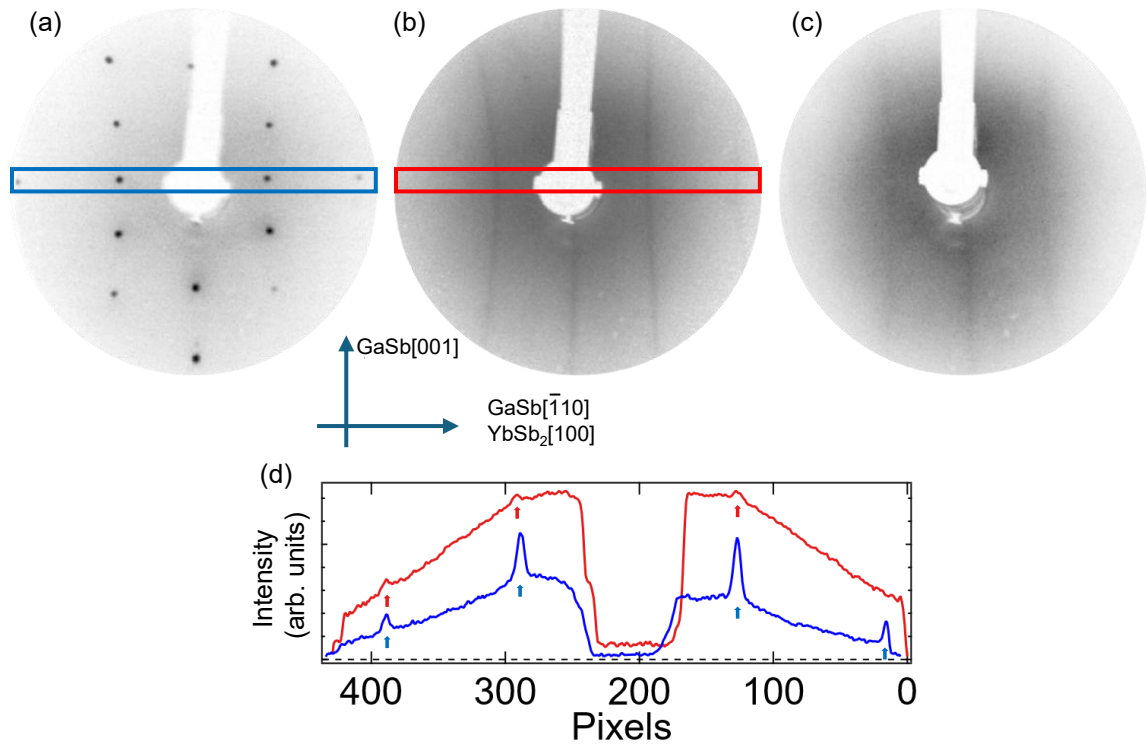


Figure 4.16: LEED patterns of (a) GaSb(110) clean surface prepared by cleaving *in situ*. (b) YbSb₂ thin film grown on GaSb(110) substrate prepared by cleaving. (c) YbSb₂ thin film grown on GaSb(110) substrate prepared by Ar-ion sputtering, measured using 110-eV electrons. (d) line profile of LEED patterns in (a) and (b) using the data in the blue and red squares, respectively.

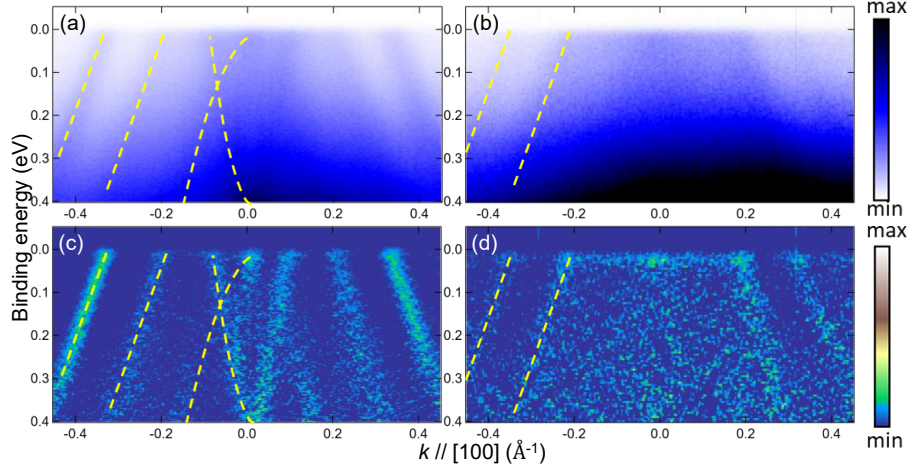


Figure 4.17: ARPES intensity plot of YbSb₂ grown on GaSb(110) clean surface prepared by cleaving in situ, measured along YbSb₂[001] direction with (a) LH 21-eV photons and (b) LV 21-eV photons. (c) The curvature plot corresponds to (a). (d) The curvature plot corresponds to (b).

Figure 4.16 (d) exhibits the line profiles of the LEED pattern of the GaSb(110) substrate and the fabricated YbSb₂ sample, using the data surrounded by the red and blue squares in (a) and (b). From the line profile, we found that the streaks and the diffraction peaks of the GaSb(110) surface have nearly the same spacing along the $[\bar{1}10]$ direction of the GaSb(110) surface. Given the atomic spacing along the $[\bar{1}10]$ direction of GaSb is $6.095/\sqrt{2} \approx 4.31$ Å, the crystalline direction that aligns with the $[\bar{1}10]$ direction of the substrate is considered to be either [001] or [100] direction with a lattice parameter of 4.268 Å or 4.561 Å. Meanwhile, because of the lack of long-range periodicity along the [001] direction of GaSb(110) substrate, the crystal direction that aligns with the [001] direction of GaSb(110) substrate could not be determined only from LEED results.

Figure 4.17 exhibits the ARPES intensity plots of YbSb₂ thin film grown on GaSb(110) substrate, together with the corresponding curvature plot. Different from the complicated bands observed in the YbSb₂(010) film grown on GaSb(001) surface, clear dispersions of three hole bands and one electron pocket that cross the Fermi level are observed, indicating the semimetallic state of YbSb₂. The electron pocket exhibits rapid dispersion with a minimum at around 0.4 eV. According to the reported calculation results [53, 54], no such electron-like band is expected to appear around the bulk Γ point, indicating that the observed electron pocket should originate from the projection of another point in the Brillouin zone because of the k_z broadening. Given that such fast electron-like dispersions only ap-

pear on the T-Z line in the bulk Brillouin zone, as shown in Fig.1.14 (b), the out-of-plane direction of the fabricated films should be coplanar with the T-Z direction. Therefore, the crystal direction that aligns with the $[\bar{1}10]$ direction of GaSb(100) substrate could be determined to be the $[100]$ direction of the YbSb₂.

4.3 Summary

In summary, we have studied the MBE growth of Yb-Sb thin films. With increasing $\phi_{\text{Sb}}/\phi_{\text{Yb}}$ ratio, in addition to the previously reported Sb-rich YbSb₂(010), the epitaxial growth of Yb-rich Yb₁₁Sb₁₀ with mixed (110) and (001) orientation was also achieved. However, YbSb was not formed in all the films fabricated in this study. The reason could be attributed to the weak electron electronegativity of Sb, which is insufficient for the YbSb with unstable trivalent Yb ions to be formed.

Also, we have grown YbSb₂ thin films on GaSb(001) and GaSb(110) substrates, and investigated their electronic structure by synchrotron-based ARPES. YbSb₂(010) with (2×1) surface reconstruction has been successfully grown on GaSb(001) substrate, where the electronic structures qualitatively consisted with the reported calculation results, with the evidence of the band folding corresponding to the (2×1) surface reconstruction observed. Meanwhile, 1D-like YbSb₂ thin film with long-range periodicity only along the $[\bar{1}10]$ direction GaSb(110) surface has been fabricated on GaSb(110) substrates, where simple dispersion with three hole-like bands and one electron pockets, which is considered to originate from the projection of the electron-like dispersion near another point in the Brillouin zone on T-Z line. The semimetallic state of YbSb₂ was indicated by the presence of both hole-like bands and an electron pocket crossing the Fermi energy, confirming the origin of the non-linear Hall effect of YbSb₂. However, the observed ARPES results do not completely reproduce the theoretical calculations [53, 54], while the reasons could be considered to be the large k_z broadening of the VUV photons, the out-of-plane momentum that is not at the high-symmetry point, and the possible material issues or limitations of the theoretical studies. Meanwhile, the details of the Dirac nodal line along the T-Z direction, which is believed to correspond to the linear non-saturating magnetoresistance in YbSb₂, were not probed in this study. These aspects remain to be further clarified in future work.

Chapter 5

Conclusion and future prospects

5.1 Conclusion

In this study, we successfully fabricated a high-quality (100)-oriented YbN epitaxial thin film for the first time using nitrogen plasma-assisted MBE. By XPS and UPS measurements, we confirmed the presence of a band gap and thus the semiconducting nature of YbN. Also, we found evidence that the Yb ions in YbN are uniformly trivalent. These findings end the debate over YbN's intrinsic properties, i.e., the semimetallic/semiconducting nature and the valence state of Yb ions, which remained unclear for many years.

On the other hand, by the growth study on the Yb-Sb system, we succeeded in fabricating Yb₁₁Sb₁₀ in the epitaxial thin-film form, which would fertilize the further studies on the properties and application of Yb₁₁Sb₁₀ based materials into thermoelectronic devices. Also, we found that in the Yb-Sb epitaxial thin-film system, as the Yb/Sb ratio increases from 1/2 to a value larger than 1, the composition changes directly from YbSb₂ to Yb₁₁Sb₁₀, with the formation of trivalent YbSb compound absent, for which the reason could be attributed to the comparatively low electron affinity of Sb and the low reactivity of Sb₄ supplied from K-cell.

Meanwhile, we fabricated YbSb₂ epitaxial thin films on GaSb(001) and GaSb(110) substrates and measured the electronic structure by synchrotron-based ARPES. On GaSb(001) substrates, (010)-oriented YbSb₂ epitaxial thin film was successfully fabricated, and band dispersions corresponding to a double period band folding were observed, which is qualitatively consistent with the reported calculation results. On GaSb(110) substrates, thin films with long-range periodicity only on YbSb₂[100] direction aligned with the $[\bar{1}10]$ direction of

GaSb(110) substrate were synthesized. From the ARPES results, both electron and hole bands crossing the Fermi level were observed, indicating the semimetallic nature of YbSb₂. On the other hand, the details of the Dirac nodal line along the T-Z direction were not probed in the recent study, and this remains to be clarified in future work.

5.2 Future prospects

In the near future, the experimental method used in this study is expected to facilitate further studies on *RE-Pns*.

Firstly, although the MBE growth of YbSb turned out to be unsuccessful using the molecular beam of Sb₄ evaporated from a normal K-cell in this study, in the similar framework to fabricate YbN with plasma assisted MBE, the usage of more reactive antimony species supplied from antimony cracker source, is expected to be a possible solution to stabilize trivalent Yb ions and thus to synthesize single crystal YbSb thin films, which deserves further exploration.

Also, the methodology of this study, i.e., a combination of synthesis of high-quality single-crystal thin film samples with photoelectron spectroscopy and other necessary measurements, is considered effective for further studies of other rare-earth pnictide systems, such as Eu-Bi or Yb-Bi compounds, which is expected to facilitate further studies not only for revealing the physical properties of rare-earth pnictide systems but also for exploring the potential applications.

In the long term, these findings are expected to generate a broader impact, advancing both the exploration of novel quantum states and their implementation in next-generation quantum devices.

A recent calculation suggested that monolayer YbN exhibits two-dimensional ferromagnetic ordering and is a promising candidate for a magnetic topological insulator with a Chern number of -1 [139]. Meanwhile, the results of this study suggest that the growth of high-quality YbN epitaxial layers by plasma-assisted MBE starts from the very beginning of deposition, indicating the possibility of synthesizing extremely thin *REN* thin-film samples, even down to monolayer thickness. Therefore, further growth studies on *REN* single-crystal thin films with reduced thickness approaching the two-dimensional limit, i.e., a monolayer single-crystal thin film, are expected to achieve the Chern insulator state, which would pro-

vide an opportunity to explore new physics such as the quantum anomalous Hall effect or even Majorana quasiparticles when superconductivity is induced.

On the other hand, ferromagnetic-insulating GdN was recently applied in NbN/GdN/NbN superconductor/ferromagnet/superconductor (SC/FM/SC) Josephson junctions, which are expected to be a promising candidate for qubits [18]. In this study, a high-quality single-crystalline thin film of YbN, which is extremely similar to GdN but exhibits an antiferromagnetic ground state, was successfully fabricated. Therefore, further investigation of the details of the magnetism of YbN thin films and the fabrication of YbN-based devices would facilitate studies of superconductor/antiferromagnet/superconductor (SC/AFM/SC) Josephson junctions, which exhibit no net magnetization or stray field. This could lead to a new type of qubit that is faster and more reliable in highly integrated quantum computing devices.

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List of publications

Refereed articles

- [a-1] **Y. Chen**, A. Meléndez-Sans, S. Kimura, L. H. Tjeng, S. G. Altendorf, “Epitaxial YbN thin films grown by nitrogen plasma-assisted molecular beam epitaxy”, *Phys. Rev. Mater.* **9**, 123403 (2025).
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